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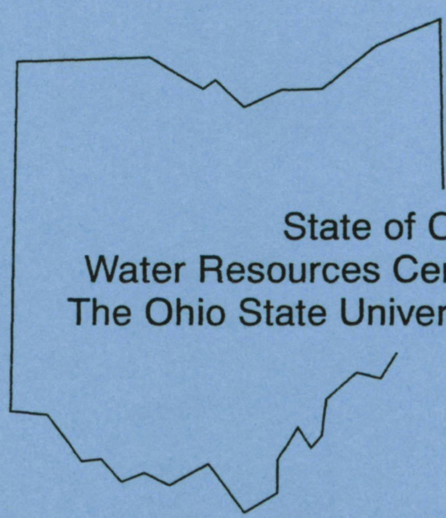
Report No. GRO-2691-03

FISCAL YEAR 1998 PROGRAM REPORT

Earl Whitlatch
Director

United States
Geological Survey



State of Ohio
Water Resources Center
The Ohio State University

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Fiscal year 1998 Program Report
Grant No. 1434-HQ-96-GRO2691

for

U. S. Department of the Interior
Geological Survey

by

Ohio Water Resources Center
The Ohio State University
Columbus, OH 43210-1057

Earl Whitlatch, Director

June, 1999

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FISCAL YEAR 1998 PROGRAM REPORT

Ohio Water Resources Center
The Ohio State University
Columbus, OH

ABSTRACT

Most of Ohio's water problems are associated with water quality. Of primary concern are the sediments, nutrients and acids in the surface waters from urban, agricultural and mining areas, and toxic and hazardous wastes that threaten the ground and surface waters. The research and technology transfer program consisted of the following activities.

One two-year research project was funded in the Regional Competition in 1996, 2 two-year projects were selected in 1997, and 4 two year projects were selected in 1998. The 1996 project by Professor Yu-Ping Chin has been extended until August, 1999. The project is "Sunlight Induced Degradation of Agricultural Pollutants in Wetlands. This research project has supported two research students in the Department of Geological Sciences at the Ohio State University. The first student won a research competition scholarship and another student has been assigned to the project.

The 1997 projects awarded in the regional competition are: Economic and Hydrologic Analysis of Integrated Wetland Reservoir and Subirrigated Agricultural Production Systems by Drs. Larry C. Brown and Marvin T. Batte of The Ohio State University, College of Food, Agricultural and Environmental Sciences. This research project provided partial support to ten students. The research project by Drs. Jonathan Levy and Robert H. Findlay of Miami University, Geology Department is: Degradation of Groundwater Quality from Pumping-Induced Surface-Water Infiltration: Bacterial Contamination. This project provided support to one Masters student in Geology

There were 4 projects awarded to Ohio in the 1998 regional competition. These projects started on September 1, 1998 and the report period ended February 28, 1999, so they had just started the research activities. They include: Sonochemical Remediation of PCB Contaminated Sediments by Linda Weavers, Civil & Environmental Engineering and Geodetic Science at Ohio State University;; Enhanced Removal of DBP Precursors During Precipitative Softening Through Co-Adsorption Processes, by Harold W. Walker of the Civil & Environmental Engineering and Geodetic Sciences Department at Ohio State University; In-situ Destruction of Solvents by Permanganate Oxidation by Franklin W. Schwartz of the Geology Department at Ohio State University; and Nutrient Cycling in Integrated Cropland/Wetland/Reservoir Management Systems by Larry C. Brown of the Food, Agricultural and Biological Engineering Department at Ohio State University.

The technology transfer program disseminated information to local and state decision-makers. Professional training and development was provided to 1,000 water resources managers throughout the year. The information transfer program has supported seminars, conferences, water education for K-12 education, provided support for professional water resource mangers and news articles for water researchers in Ohio. There were two Facilitator Workhops for 70 educators, and 47 six-hour workshops.

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Water Problems and Issues in Ohio

Water is one of Ohio's most important natural resources. Bounded on the north by Lake Erie and on the south by the Ohio River and containing other extensive ground and surface waters, Ohio generally has an adequate supply of water to meet its immediate needs. However, the combination of large, heavily industrialized urban centers; extensive agricultural activities; high volume coal production and large coal reserves; and the associated demands of new energy production continues to cause concerns related to water quality and water management. In addition, extreme hydrologic events cause localized problems of both excessive water and deficiencies at times.

Program Goals and Priorities

The 1998 program objectives as outlined by recent legislation is to:

A. Conduct research relative to important water resource problems of the Region
B. Promote the dissemination and application of the results of the research involving these problems; and
C. Assist in the training of scientists in relevant water resource fields.

Regional Research Priorities

1. Wetlands processes and management
2. Watershed processes and management
3. Drinking water quality and availability and source protection
4. Wastewater treatment for small communities
5. Urban water infrastructure
6. Non-point source pollution reduction - better management practices
7. Groundwater and surface water quality
8. Remediation of contaminated sources
9. Conjunctive use - ground and surface water interface or connectivity
10. Irrigation systems and water-use efficiency
11. Atmospheric contamination of water sources

Research proposals that include a strong educational component (student support) and/or those which have faculty beginning their careers receive some preference.

SYNPOSIS

Project Number: C-02 Start: 09/96
End: 08/98

Title: Sunlight Induced Degradation of Agricultural Pollutants in Wetlands

Investigators: Yu-Ping Chin, The Ohio State University

Congressional District: Fifteenth

Focus Categories: WL, NPP, WQL

Descriptors: Wetlands, Water Quality Control Pesticides, Nonpoint Source Pollution, Water Quality, Photolysis

Problem and research objectives:
Non-point source contamination is difficult to control because it may be distributed across large areas of the watershed. Wetlands, however, may provide a means of managing water quality since the hydrology of a watershed will often result in the collection of water from diffuse sources into basins before final discharge to other receiving waters. Numerous researchers have noted an improvement in water quality as water passes through wetlands, and have attributed this phenomenon to a combination of physical and chemical removal mechanisms.

In wetland surface waters, sunlight induced reactions may have a significant contribution to the chemical transformation of agricultural pollutants. Wetlands generally have large surface areas and shallow depths that would allow significant sunlight exposure and penetration throughout the water column. Thus, wetlands may provide an important medium for commonly used agricultural chemicals to undergo **direct** phototransformation (Simmons and Zeep, 1986; *Hwang et al.*, 1987). Moreover, wetlands, in comparison to other water bodies, are rich in photosensitizers, e.g., dissolved organic carbon (DOC) and nitrate, which are capable of absorbing sunlight and catalyzing the transformation of organic compounds by **indirect** photolysis. Valentine and Zepp (1993) have attributed observed high near-surface photoreactivity in wetlands to high levels of DOC.

Objectives: The focus of this research is to examine and evaluate the photolytic transformation of non-point source pollutants in wetland surface waters. Specific objectives of this research are as follows:

- elucidate the role of direct photolytic degradation of some commonly used agrochemicals (carbaryl, atrazine, and alachlor) at wavelengths present in sunlight;

- quantify and qualify the reactants (i. e., potential photosensitizers and transient quenchers) found in a chosen wetland site;

- conduct photodegradation experiments in the presence of these reactants from this site;

- characterize the chemical kinetics and mechanisms of these direct and indirect photolytic processes.

Carbaryl was chosen because it is a widely used carbamate insecticide in Ohio (USGS, http://water.wr.usgs.gov/cgi-bin/switch/use.cgi) and capable of participating in direct (Zepp and Cline, 1977) and indirect photolysis (through its reaction with HO*) (Mabury and Crosby, 1994).

Methodology: **Collection of Wetland Raw Water**. The field site selected for sampling wetland surface water was Old Woman Creek Estuarine Reserve (OWC) which is a 30 hectare wetland located on the south shore of Lake Erie, 5 km east of Huron, OH (Figure 1; web page reference). Approximately 69 km^2 of agricultural land drains into OWC's basin and subsequently, it receives a significant amount of suspended solids and pesticides (D. Baker, personal communication). Sampling sites were chosen at the inlet, interior (railroad, and outlet of the wetland. Samples were collected on June 17, 1996, which corresponded to the time of spring runoff (Kreiger, personal communication), and August 7, 1996. Raw water samples were collected in 4-L amber glass jugs. placed on ice, and transported to OSU. Samples were stored at 4°C until used.

Characterization of Wetland Raw Water. Wetland water samples were filtered through a glass fiber filter (Gelman A/E) prior to analysis and use. Samples were analyzed for dissolved organic carbon (DOC) using a Shimadzu TOC 5000 Analyzer. The light absorbing properties of the DOC were assessed with UV/VIS spectrophotometry (Varian Cary 1). Samples were scanned in quartz cuvette from 200 to 600 nm. The collected absorptivities were used to calculate attenuation coefficients and light screening factors appropriate for each natural water sample. Samples were analyzed for nitrate via reverse phase high pressure liquid chromatography (HPLC) (Schroeder, 1987). The limit of detection for nitrate in the wetland water samples was at 2.0×10^{-6} einsteins/sec/L.

Reaction mixtures were prepared by spiking 50µL of carbaryl stock solution (in acetonitrile; 5×10^{-3}M) to 50 mL of either phosphate buffered MilliQ water (MilliQ water system, Millipore Corp., Bedford, MA) or filtered OWC water yielding a nominal carbaryl concentration of 5 µM. Two mL aliquots of reaction solution were pipetted into pyrex culture tubes (13 x 100 mm) and were either stored in the dark in a temperature controlled water bath or irradiated at λ= 366 nm at a temperature of 27.5°C. Test tubes were sacrificed periodically during the irradiation, and the reaction was quenched by the addition of 2 mL of acetonitrile and storage in the dark at 0°C. Stability studies showed that samples may be stored up to 14 days without any significant degradation. Samples were assayed by HPLC for the parent compound and the detectable derivative (1-naphthol). A direct aqueous injection (25µL) from each vial was made into the HPLC and analytes were detected with a programmable fluorescence detector (Waters 470). The mobile phase for the analysis was 37% acetonitrile: 63% MilliQ water, and the flow rate was 1.5 mL/min. The program for the detector was: initial through 4 minutes, $\lambda_{excitation}$ =282 nm, $\lambda_{emission}$ = 330 for carbaryl (RT=3.4 minutes); 4 minutes through 5.5 minutes, $\lambda_{excitation}$ = 292nm, $\lambda_{emission}$ = 462nm for 1-naphthol (RT=4.5 minutes). Preliminary work in our lab have shown that this analytical approach is highly sensitive and provides linear detection over several decades of analyte concentration.

Radical Trapping Experiments. Experiments were performed to quantify the level of hydroxyl (HO*) radicals produced through the indirect photolysis of OWC water according to the radical trapping methods of Vaughan and Blough (1998). Standard solutions of 3-amino, 2,2,5,5-tetramethyl pyrolidinoxy free radical (3-AP; 50 mM in MilliQ water) and fluorescamine (5nM in acetonitrile) were prepared weekly and daily, respectively. All standards were stored in the dark. To 2mL of sample, 1.4µL of DMSO and 2µL (anaerobic) or 10µL (aerobic) of 3-AP solution were added. Reaction solutions and appropriate blanks were irradiated. After irradiation, the pH was adjusted to 8 (if necessary) and 1mL of solution was withdrawn and derivitized with 200µL of the fluorescamine standard. Derivitized samples were analyzed via HPLC using a mobile phase of 65% methanol: 35% sodium acetate (50 mM, pH-4) at a flow rate of 1mL/min. The produce was detected by fluorescence (390 nm excitation and 490nm emission) with a retention time at 7 minutes. A 3-AP fluorescamine method adduct synthesized in our lab was used to generate a calibration curve.

Data Analysis. Data were analyzed using *Scientist for Windows* v. 2.01 (MicroMath Scientific Software, Salt Lake City, UT). Rate expressions describing the observed kinetics were solved numerically using the EPISODE package, and observed rate constants for carbaryl degradation were determined from least squares fit. (Powell algorithm) of the observed kinetic data to the pseudo-first order kinetic model. We did not consider it necessary to correct for carbaryl binding to dissolved organic matter since carbaryl has a relatively high solubility (0.05 g/L@ 20° C), and calculations based on the reported organic carbon partitioning coefficient (205-457 L/kg) showed that no less than 0.7% of the carbaryl spiked into the solutions would be associated with the organic matter present in the OWC water. Also, we did not correct for the partitioning of carbaryl into the headspace of the test tubes since carbaryl has a low Henry's law coefficient ($10^{-1.1}$ atm L/mol).

Principal Findings and Significance:

Several water quality parameters (e.g., pH, DOC, nitrate, alkalinity) were measured for the OWC samples (Table I). The UV/VIS absorption spectrum for each OWC sample was also recorded (Figures 2 and 3). The spectra of the June samples were dominated by the presence of nitrate (see insert # 2 in Figure 2) as expected based upon the measured concentrations of nitrate in these samples (Table I). For the August samples, spectra more characteristic for DOM present in natural water samples were obtained.

Normalized (to the total amount of carbon present) molar absorptivities (ε) at λ=280 nm may indicate the amount of aromatic carbon present in natural water samples (Gauthier *et al.*, 1987; Traina *et al.*, 1990; Chin *et al.*, 1994). The low molar absorptivities (corrected for nitrate absorbance at 280 nm) observed for OWC water suggests that this material contains few aromatic moieties. As a comparison, International Humic Substance Society (IHSS) fulvic acids isolated from "blackwater" wetlands possessing high aromaticity (i.e. Suwanee River) have extinction coefficients at 280 nm at least 2 x's greater than those measured here (Chin *et al.*, 1994). Moreover, even though the amount of DOC almost doubles in the water al all sites between June and August, ε remains approximately the same; thus, we believe that input of new NOM over time does not change its structural character. The normalized absorptivity, however, does decrease for both sample sets from the inlet to the outlet which suggests that the aromatic character of the NOM decreases as water passes through the wetland.

Previous results indicated that direct photolysis of carbaryl between λ = 290-360 nm may be a very efficient process (Armbrust and Crosby, 1991). Since our objective in this study was to identify the wetland water constituents participating in indirect photolytic processes, we chose to study photolysis at a wavelength (λ = 366nm) where direct photolysis of carbaryl would be minimized (due to a small extinction coefficient) but the natural water was still able to attenuate light. Thus, we planned for the experimental conditions to favor indirect photolytic pathways, if any light enhancement was to be observed. The absorbance at λ =366 nm was recorded to calculate the appropriate screening factors expected for each natural water sample during the photoreactions (Table I). The light screening factor (S_λ) can be used to correct the effect of light attenuation by natural waters on the direct photolysis rate. Application of S_λ to rate constants measured in distilled water can yield upper limit estimates of expected photolysis rates in the natural waters under same irradiation conditions. For the OWC water, S_λ ranged from 0.94-0.97 and indicated that light attenuation by natural water constituents would compete for only 3-7% of the photons impinging the samples in these laboratory experiments.

Results of Kinetic Studies: Rate constants were treated according to pseudo-first-order kinetics, and models fit reasonably well having R^2's>0.99 for all reactions (e.g., Figure 4). The dark reaction for carbaryl in the natural water systems was shown to be quite significant (Table II). This result is not unexpected as carbaryl is known to undergo a significant base-catalyzed elimination reaction at pH's greater than 7 (Aly and EL-Dib, 1971a, b; Wolfe *et al*, 1978). Since the pH of the OWC water was found to be greater than 8 for all samples, contribution from the dark reaction would be large and , in fact, accounted for the largest percentage of the overall reaction in the light (Table II).

The light induced degradation of carbaryl was 1.1 to 1.4 x's higher than that in the dark for some of the natural water samples (Table II). Thus, the presence of light at λ = 366 nm did enhance carbaryl's degradation. The only daughter product observed and quantified was 1-naphthol (Figure 4). In the dark reactions, 1-naphthol accumulated in the solution phase resulting in good mass balanced (Table II). Conversely, in the photoexperiments, 1-naphthol behaved as an intermediate and never accumulated to levels observed in the dark; thus, mass conservation based on this derivative alone was never achieved (Table II).

The contribution of any known environmental process to an observed rate of disappearance (k_{obs}) may be quantified by comparing the relevant first or pseudo-first order rate constant for the process in question (k_j) to the sum of the relevant rate constants (i.e., Σk_j). Thus, the measured rate constant for the photoreaction of carbaryl in OWC water can be expressed as:

$$k_{obs} = \Sigma k_j = k_{OH-}[OH-] + k_{direct} + \Sigma k_j [transient]_j \qquad (1)$$

where k_{oh-} is the second-order rate constant for the base-promoted elimination reaction, k direct corresponds to the relevant rate constant for the direct photolysis, Σk_j are the second-order rate constants for any reactive transient species *i* that results in the indirect photolysis of carbaryl.

From 5-24% of the **overall** reaction for the natural water samples showing light enhancement could be attributed to light induced pathways (direct and indirect). Under the assumption that the pH does not affect the direct photolytic pathways (Wolfe *et al.* 1978) the light screening factor can be applied to the measured direct photolysis rate constant (0.0034 hr^{-1}) obtained from an experiment conducted in MilliQ water to yield a predicted direct photolysis rate for each OWC sample.

The rate constants measured for waters showing significant light enhancement could be attributed to light induced pathways (direct and indirect). Under the assumption that the pH does not affect the direct photolytic pathway (Wolfe *et al.* 1978) the light screening factor can be applied to the measured direct photolysis rate constant (0.0034 hr^{-1}) obtained from an experiment conducted in MilliQ water to yield a predicted direct photolysis rate for each OWC sample.

The rate constants measured for waters showing significant light enhancement exceeded the simple sum of the k_{dark} and k_{direct} and indicated that indirect photolytic processes are important for these water samples. Subtraction of k_{dark} and k_{direct} from k_{obs} yielded a pseudo-first order rate constant that is representative of the indirect photolytic processes may account from as little as 1 % up to 23% the overall reaction in light and were apparently far more important in the June inlet and railroad samples than in the August inlet and railroad samples.

Effect of Natural Water Constituents: The possible reasons for the large range of reactivity should be interpreted within the context of the water samples. Analysis of the surface water revealed two possible photosensitizers: nitrate and natural organic matter (NOM). Nitrate is capable of producing hydroxyl radicals (HO•) with quantum yields ranging from 0.08-0.015 when irradiated from 298 to 371 nm, respectively (Mabury and

Crosby, 1994). Conceivably, in wetlands that receive agricultural runoff, nitrates may be sufficiently high enough to influence contaminant photolysis. Nitrate levels monitored in OWC from 1988-1990 ranged from 0.032-2.0 mM (Krieger, personal communication) and correspond well to this study (Table I). At the nitrate levels found in this study (7.9×10^{-5} -4.7×10^{-4}M) the predicted production (noon-day sunlight at 40°) of relatively high steady-state concentrations (~10^{-15} -10^{-17}M) (calculated from Schwarzenbach *et al.*, 1993) of HO• may be important in OWC compared with other water bodies (~10^{-18} -10^{-16}M) (Zepp *et al.,* 1987). Indeed, radical trapping experiments showed that almost 10^{-16} M of HO• were produced in OWC water with total nitrates around 1mM after sixty minutes of irradiation at λ = 366nm (White and Chin, unpublished data). This level is equivalent to the upper limit of HO• measured in natural waters irradiated with noon-day sunlight.

A correspondence between nitrate level and observed reaction rate constant in the light was observed (Figure 5); the samples that showed the most significant light enhancement contained the highest levels of nitrate. The observed pseudo-first order rate constant, k_{obs}, decreased as nitrate level decreased through the wetland in the June samples (inlet to outlet). In the August samples, nitrate level was significantly lower, and it s role as a photosensitizer would be expected to be significantly diminished.

Other water constituents may significantly influence the nitrate driven photochemical production of HO• available for pollutant transformation. Indeed, in considering the samples that showed light enhancement, the DOC level seems to be inversely related to the measured k_{obs} (Figure 5). Since the OWC water had a relatively high alkalinity with total carbonate levels generally exceeding DOC by nearly an order of magnitude in some cases (depending on the water sample), carbonate species are probably the principle HO• scavengers for this water. As HO• is scavenged, the measured degradation of carbaryl with time would be expected to decrease. NOM has also been reported to quench excited states and scavenge reactive intermediates and photons (Miller *et al.*, 1980; Hwang *et al.*, 1987; Larson and Zeep, 1988; Woodburn *et al.*, 1993). As a consequence, very low steady-state concentrations of these reactive species in natural surface waters have typically been observed (Faust and Hoigne, 1987).

Control photolysis experiments were performed to determine the influence of nitrate photochemistry on the photoinduced degradation of carbaryl. Photoreactions were performed in carbonate buffered ($(CO_3^{2-})_T$=3.6mM corresponding to the average amount measured in the OWC water) MilliQ water and OWC water at a pH (6) sufficient to inhibit the dark reaction pathway (Figure 6). In the "clean" (no NOM present) experiments, the effect of adding 0.40 mM nitrate to the solution enhanced the photolytic reaction by a factor of 6 compared to the MilliQ control. Experiments with pH adjusted OWC water also showed that when the Outlet (June) same (low nitrate) was "spiked" with NO_3 (to levels observed at the Inlet site) the indirect photolysis component increased to a level similar to that observed in the OWC Inlet (June) sample (Figure 6).

Effect of Daughter Products on Photodegradation. Finally, the production of 1-naphtol during the reaction may also affect carbaryl degradation. A plot of 1-Naphthol concentration versus time showed intermediate behavior and may indicate its participation in photochemical reactions. Photochemical reactivity of 1-Napthol could influence the fate of carbaryl through a number of mechanisms. First, as this daughter product accumulates, it may compete with carbaryl or other photoreactive water constituents for photons, thereby inhibiting carbaryl degradation, Conversely, 1-naphthol may act as a photosensitizer to enhance carbaryl degradation. Control experiments were performed to test what the effect of 1-naphthol might have on the degradation of carbaryl. In phosphate buffered solutions (pH=8.5), 1-naphthol was added at various molar ratios to a solution of carbaryl (5 μM) (Figure 7). The addition of 1-naphthol enhanced carbaryl degradation but there did not seem to be a statistical difference between the level of enhancement and the molar ratios tested. Therefore, taking the average of the results, 1-naphthol enhanced the carbaryl degradation by almost 25 percent. AN important factor in determining the significance of this enhancement in natural waters will be the pH. The higher the pH, the faster the dark reaction will proceed to produce 1-napphthol which, in turn could react to degrade carbaryl.

Effects of pH on the Photodegradation. In order to assess the kinetics of carbaryl's photoreaction, the assumption was made that the direct photolysis rate was independent of the pH. While this assumption was shown to be true for certain natural waters tested in the pH range from 6-7 (Wolfe et al., 1978), other studies showed a pH-dependent photolytic mechanism (Aly and El-Dib 1971b; Wauchope and Haque, 1973) at higher pH's. In order to investigate this assumption carbaryl was irradiated at several pH's ranging from 6-8.5 with λ=366 nm light. Rate coefficients and quantum yields measured were found to be positively correlated to the pH (Figure 7). While this dependency will not be significant at lower pHs (see insert Figure 7), it may have a significant effect in enhancing carbaryl's direct photodegradation rate in more alkaline natural waters such as OWC or ORWRP.

SUMMARY

Indirect photolytic pathways influenced the photodegradation of carbaryl in a natural wetland surface water when irradiated at λ = 366 nm. Levels of HO• produced from irradiation of the OWC water at λ =366 nm approached the upper limits measured for other natural waters irradiated with the full spectrum of sunlight. The enhancement by light appears to be related primarily to the concentration of DOC, alkalinity, and nitrate. The alkalinity of the water primarily quenched the photolytic reaction. To our knowledge this study is the first to observe that levels of nitrate actually occurring in natural water influenced the extent of the indirect photolysis of a contaminant. The amount of nitrates and nitrites present in wetlands such as OWC will be largely dependent upon the amount of agricultural runoff and municipal inputs into the system and the degree of cycling that occurs by phytoplankton, microorganisms, and higher plants. Conceivably, nitrates in certain wetlands could be sufficiently high enough to impact contaminant photolysis if other scavengers such as carbonates and NOM concentrations are relatively small (e.g., cranberry bogs in the Northeast). Direct photolysis of carbaryl was found to be pH dependent.

Because we chose to study the photodegradation of carbaryl at one wavelength (366 nm) present in surface sunlight, we would expect that the extent of photo enhancement would be minimized compared to what we would see in the full spectrum of sunlight. We expect that further studies conducted in sunlight will show an acceleration of the observed degradation, and are currently planned. Future research must also include the positive identification of the other daughter species besides 1-naphthol. Identification and quantification of daughter species should help to elucidate the pathways of different mechanisms. These products are also being tested for possible autocatalytic influences on the reactions.

Other results and Future Work: Atrazine showed little degradation when exposed to sunlight in quartz tubes in OWC water. A recent publication by Torrents *et al* (1997) comprehensively examined the photochemical degradation of atrazine in a natural water spiked with nitrate (mechanisms and rates); thus we are currently restructuring our planned activities concerning this compound. The water quality parameters for ORWRP water sampled from the inlet and outlet are being characterized and will be compared to findings from OWC water. Future studies are planned to quantitate the role indirect photolysis plays in the decomposition of carbaryl, and eventually, alachlor in these different surface waters.

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Publications:

1. ARTICLES TO BE PUBLISHED IN REFEREED SCIENTIFIC JOURNALS

Miller, Penney, L., Yu-Ping Chin, 1998, Photoinduced Degradation of Carbaryl in a Wetland Surface Water, in *preparation to be submitted to Environmental Science and Technology.*

Miller, Penney, L., Yu-Ping Chin, 1998, Mechanisms Governing the Photochemical Transformation of Carbaryl in Aqueous Systems, *in preparation to be submitted to Environmental Science and Technology.*

2. CONFERENCE PROCEEDINGS

Miller, P. L. and Chin, Y. P. (1997) "Photoinduced Degradation of Organic Pesticides in Wetlands", *SETAC National Meeting*, San Francisco, November, 1997.

Miller, P. L. and Chin, Y. P. (1997) "Photoinduced Degradation of Agricultural Pollutants in Wetlands", *American Chemical Society National Meeting*, San Francisco, April, 1997.

Miller, P. L. and Chin, Y. P. (1996) "Photoinduced Degradation of Agricultural Pollutants in Wetlands", presented at the *19th Annual Midwest Environmental Chemistry Workshop*, October 12-13, West LaFayette, IN.

SYNOPSIS

Project Number: C-03

Start: October, 1997
End: December 1999

Title: Economic and Hydrologic Analysis of Integrated Wetland Reservoir and Subirrigated Agricultural Production Systems

Investigators:
Larry C. Brown, The Ohio State University
Marvin T. Batte, The Ohio State University

Congressional District: OH 15

Focus Categories: WL, HYDROL, ECON

Descriptors: Constructed wetlands, subirrigation, hydrology, agriculture, economics, water table management, water level and quality control, water harvesting and conservation, solute transport, ecosystems, agroecosystems, education, hydraulics, drainage management, impoundments, information dissemination, irrigation and management, land-water interactions, perched water table, ponds, reservoir development and management, sedimentology, storm water management, nutrient delivery to streams, sediment, runoff, subsurface drainage, surface drainage, controlled drainage, near-surface ground-water levels, hydrologic and ecosystem models, Great Lakes, water reuse and recycling, landscape and watershed management, off-site impacts, management, modeling, and monitoring, water resources development, water use monitoring.

Problem and research objectives:

The Maumee River valley is characterized by flat topography with soils that are predominantly heavy clay - glacial deposits and lakebed sediments. Extensive drainage projects have permitted the area to be drained, cleared, and farmed, resulting in a very productive farming region, but one which is very dependent on surface and subsurface drainage improvements. Drainage discharge enters the Maumee River and Lake Erie as a result of intensive drainage improvements. Sediment, phosphorus, nitrate, and certain pesticides in agricultural runoff are of great concern in the region. No research has been conducted on hydrologic interactions within the direct linkage of an agricultural production system and a wetland-reservoir ecological system, nor the economics of such a system.

An existing demonstration project (funded by USEPA/GLPO and others) demonstrates construction and management of permanent wetland-reservoirs linked directly to subirrigated corn and soybean production systems on field-sized areas. The demonstration project was initiated in 1994 to illustrate how construction and management of wetlands coupled with subirrigation can be economically profitable for farmers. The overall objective of the demonstration project is to stimulate adoption of wetlands, reduce adverse impacts of agricultural runoff, and maintain profitability. The project was built on the need to enhance and properly utilize wetlands near agricultural land use areas where the success of subirrigation has a high potential.

The WRRI project adds important economic and hydrologic research components to the existing Maumee River valley demonstration project. This productive farming region is very dependent upon drainage improvements, which discharge to the Maumee River and Lake Erie where sediment, phosphorus, nitrate, certain pesticides in runoff are of concern. Runoff and drainage from prior converted cropland will seasonally feed wetland-reservoirs, which provide water quality and wildlife habitat functions, and supplemental water supply for state-of-the-art subirrigated crop production systems. Construction and management phases for three wetland-reservoir-subirrigation sites are funded (operational for 1996 growing season) and complete. Research was needed on hydrologic interactions within the direct linkage of agricultural production systems and wetland-reservoir ecological systems, and the economics of such systems. Currently, no work of this focus and extent is being conducted elsewhere in the U.S.

Research Objectives

Objective 1: Characterize, analyze, model hydrologic interactions between integrated subirrigated agricultural production and constructed wetland-reservoir systems, and evaluate the water quality (sediment, pesticide, nitrate and phosphorus transport) impacts and benefits of this integrated system.

Objective 2: Examine and determine farm-level economics of integrated subirrigated agricultural production and constructed wetland-reservoir systems.

Technology Transfer Objective

Objective 3: Develop a technical design and management guide for subirrigated agricultural production and constructed wetland-reservoir systems, and conduct an applications and design workshop to teach agricultural producers and consultants how to use water table management for environmental and economic benefit.

Methodology:

Existing Funded Demonstration Project

Wetlands have been constructed on prior-converted cropland to receive drainage from adjacent cropland, resulting in zero-discharge from those fields directly to streams. Agricultural runoff and subsurface drainage will recharge the constructed wetland seasonally during periods. The wetland-reservoir water will be recycled through a subirrigation system, thereby providing a supplemental water supply for subirrigating corn and soybean crops in adjacent fields. In a year with average rainfall, the system should produce a zero discharge to streams and rivers which will greatly aid in improving water quality, reducing peak flows, and at the same time form permanent pools for increased wildlife habitat areas. Substantial subirrigation research on corn and soybean conducted in Michigan and Ohio suggests a strong potential for northwestern Ohio, but often water supply is a limiting factor.

The soils and topography are those that will respond to subsurface drainage improvement, subirrigation, and constructed wetlands. Cropping and management plans for the entire farm include agricultural practices used in accordance with an approved conservation plan as prepared by USDA-NRCS, with a landowner commitment of five years minimum. Each landowner is required to provide information on all inputs and outputs, and follow the water management plan and the cropping management plan established by the project team (contract established between demonstration project and landowner).

The systems were designed using research results and inputs from the USDA-ARS Soil Drainage Research Unit; Michigan State University - Department of Agricultural Engineering; The Ohio State University, Department of Food, Agricultural, and Biological Engineering, Ohio Agricultural Research and Development Center, and Ohio State University Extension; and technical assistance from the USDA-NRCS and the Ohio and Michigan Land Improvement Contractors' associations. The Maumee Valley RC&D coordinates all specific tasks with the main sponsors (USEPA/GLPO; Lake Erie Protection Fund, etc.), and all collaborators.

The WRRI funded research focuses on all 3 sites: Defiance Agricultural Research Association (DARA) site (near Defiance County airport and weather station); Fred Shininger farm (Fulton County); and March Foundation (Van Wert County near Farm Focus), but the main focus of the intensive monitoring and research is at the DARA site. Each site consists of a subirrigated area for corn and soybean production, constructed wetland, and constructed upground reservoir (or existing pond). Runoff and subsurface discharges from adjacent cropland flows into the constructed wetland. Once water flows out of the wetland, it is pumped to the upground reservoir where it is stored for water supply. During the crop season, water is pumped into the subirrigated cropland, where a water table is held at a 14- to 20-inch depth throughout most of the growing season. Each site will have numerous locations to measure and sample surface and subsurface flows, subirrigation water use, runoff, etc., and are being instrumented so that water flow rates and volumes, and sediment and chemicals concentrations can be measured at the inflow and outflow of each component of this integrated system.

Runoff and subsurface discharge will be monitored and evaluated during and after all storm events (possibly 10 to 20 storm events annually), and during selected less dynamic times throughout the year. One-liter water samples will be collected during flow events. For two selected storm events per year, more intensive sampling will occur to establish the water and chemical discharge relationship with time for the entire rainfall event. All samples will be analyzed for nitrate+nitrite, soluble phosphorus, and selected pesticide concentrations by the Water Quality Laboratory at Heidelberg College in Tiffin, Ohio, and the MSEA Water Quality Lab at Ohio State University following MSEA QA/QC procedures. All concentration data will be analyzed on a flow-weighted basis. For the recessional limb sampling, the number of samples collected each year will be approximately 90 (up to 20 events per year, at up to six sampling locations). For the full storm duration sampling sequence, approximately 80 samples will be collected per year (20 samples per selected storm event per year for both drainage treatments). Sediment samples will be analyzed locally by gravimetric means. Wetland and reservoir sedimentation will be assessed annually.

Inflows and outflows from each flow control point will be measured at time of sampling. In addition to the installation of commercial flow rate and volume measurement devices, the drainage control structures will be modified with a V-notch weir for flow rate estimation at the time of sampling, thus producing a redundant volumetric sampling. Runoff entering the wetland area will be monitored using H-flume and stage recorder systems. Within each field area, simple water table observation wells will be installed between laterals near each outlet to allow monitoring of water table elevations. Rainfall at each site will be measured using manually read rain gauges, and local weather records are available in each county. Daily measurements of water table elevations, flow rates and volumes, etc. will be made by the demonstration project personnel.

All management and data collection at all three sites is fully funded through the existing project through the 1999 crop season, and is managed by a team of farmers, state and federal agency personnel, and university faculty. All instrumentation and data collection procedures are being designed by Dr. Brown, in coordination with the demonstration project team. Each site has unique characteristics that allow excellent research opportunities over a range of conditions.

<u>Objective 1: Characterize, analyze, model hydrologic interactions between integrated subirrigated agricultural production and constructed wetland-reservoir systems, and evaluate the water quality (sediment, pesticide, nitrate and phosphorus transport) impacts and benefits of this integrated system.</u>

Substantial soils, topographic, cropping system, water budget, sediment and chemical data, and engineering design information, will be generated from the existing demonstration project. Much of this information and data will be used to calibrate existing, state-of-the-art agricultural water management models and design techniques that will be modified to analyze and evaluate hydrologic interactions between these systems (discussed below).

Soil characteristics (profile description, textural analysis, hydraulic conductivity, etc.) will be measured at each site. In addition, each field-sized research area were hydraulically characterized before the actual design, construction and implementation of subirrigation. All crop production and land management conditions will be the same on both the subirrigated and non-subirrigated areas. Crop growth and production characteristics (leaf area index, height, canopy, yield, etc.) will be measured during each crop season. Crop yield, crop production management, tillage, and nutrient and pesticide application data will be collected from each cooperator. A water table management scenario will be established at each demonstration site in consultation with the demonstration project technical advisory committee, and based upon recommendations by Cooper and Fausey (1991; 1992).

Dr. Brown and the engineering graduate associate will conduct the research that addresses Objective 1 using the agricultural water management simulation models DRAINMOD (Skaggs 1980; Skaggs et al. 1981), ADAPT (Agricultural Drainage and Pesticide Transport) (Chung et al. 1992a; Chung et al. 1992b), and possibly the new USDA erosion model WEPP (Water Erosion Prediction Project). These hydrologic and erosion prediction models will be used to conduct computer simulations using long-term climatic records to evaluate the hydrologic and crop production potential of the soils at all three demonstration sites for subirrigation and drainage collection in the study area. These hydrologic models have the ability to evaluate subirrigation scenarios, and can be used to analyze and evaluate these integrated systems over time using historic climatic records. Both DRAINMOD and ADAPT have the capability to simulate water table elevations, surface and subsurface movement of water on agricultural soils that are not drained, and for water table management conditions with conventional subsurface drainage, controlled drainage, and subirrigation. Long-term subsurface discharge, runoff, evapotranspiration, water use, water table elevation, and other water budget parameter estimates, as well as crop yields, will be statistically evaluated. In addition, sediment, pesticide, nitrate and phosphorus movement from all three sites will be evaluated using the ADAPT model.

For use with DRAINMOD and ADAPT, soils data have been obtained at each site, from the state's Soils5 data base (Baumer, 1989), and county soil survey manuals. In addition, hydraulic conductivity and topographic information from each demonstration site has been obtained for our use. Climatic data (hourly precipitation, max/min daily temperatures) with a minimum of 30 years of record (forty year records are being developed) for at least four northwest Ohio locations have been obtained and formatted for DRAINMOD. These records will be modified for input to ADAPT so that each model will use the same soils and climatic data

The DRAINMOD and ADAPT models produce similar predictions of water table elevations on agricultural land use areas (Desmond et al. 1994), and both models have been tested on Ohio conditions. DRAINMOD currently does not have the capability to predict water quality impacts (sediment, nitrate, phosphorus, pesticide transport). However, the ADAPT model has the capability to model erosion processes, and based upon algorithms adapted from the GLEAMS model (Knisel et al. 1992), it can model nitrate and phosphorus transformations and transport. ADAPT will be used in this study to assess the hydrologic, erosion, runoff, subsurface drainage, and crop yield potential of water table management practices for the demonstration site soils. Because of its wider acceptance throughout the United States to evaluate the hydrology of agricultural land use areas and wetland hydrology, DRAINMOD predictions will be used simultaneous to ADAPT as a control. For the conditions at each demonstration site, long-term simulations will be used to develop matrices of crop yield, nitrate and phosphorus transport relationships, thus allowing the research team to assess the relationship of the economic and water quality benefits of these integrated subirrigated - constructed wetland-reservoir systems.

The USDA erosion model WEPP (Water Erosion Prediction Project) is being evaluated for its application to this project..

Objective 2: Examine and determine farm-level economics of integrated subirrigated agricultural production and constructed wetland-reservoir systems.

The long-term economic performance of integrated subirrigated agricultural production and wetland-reservoir systems investments relative to systems with no subirrigation-wetland linkage will be analyzed and evaluated. Net present value techniques will be used to value profitability, and linear programming techniques will be used to compare differences in profitability reflecting differences in farm size under the two production systems. Actual capital investments for design and construction will be obtained from each demonstration site. Estimates of the useful life of each component of the system and maintenance costs will be made, and actual production costs, yields, and returns will be collected for production of each crop at each site. Historical yield and cost data will be gathered for each site for years prior to the wetlands development. These data will be the basis for comparison of economic costs and returns for each site, prior and subsequent to the wetlands-subirrigation investment. In addition, Drs. Fausey and Cooper, and the Michigan State cooperator, respectively, have agreed to provide selected Ohio and Michigan water table management system cost and return economic data. For comparison, we are currently evaluating the subsurface drainage yield response data from two long-term projects in Ohio.

Dr. Batte and the agricultural economics graduate associate will assess the economic performance of subirrigation technologies. Enterprise and whole-farm budgeting techniques will be used to examine the impact of the subirrigation investment for typical Ohio commercial farms. Because these investments involve long-time durations, capital budgeting techniques also will be used to reflect differences in timing of receipts and expenditures. Additionally, mathematical programming techniques will be used to compare the economic performance of a representative farm with and without subirrigation improvements. Enterprise and whole-farm budgets will be constructed for representative farms under two scenarios: 1) with a conventional subsurface drainage system designed to be optimal for prevailing soil conditions, and 2) with a subirrigation system, again designed to be optimal given existing soils.

Simple budgeting analyses as described above and reported in a number of empirical studies (Evans et al. 1988; Rath and DeBoer 1991; Belcher 1992; and Drouet et al. 1989) do not provide a complete analysis of profitability differences among systems. The reason is that there may be changes in a great number of other aspects of the business resulting from the subirrigation investment. Positive impacts may include farming of larger acreage, incorporation of higher-valued (but previously infeasible) crops into the rotation, greater specialization in the highest-valued crop, or reduced hiring of labor during critical periods for field operations. Negative impacts might include increased competition within the business for scarce capital resources and associated loss of production efficiency or business size.

Linear programming models will be constructed for representative farms in northwestern Ohio. At each site, one model will feature crop production on representative soils with conventional subsurface drainage. A second model will consider the addition of a subirrigation system that will provide supplemental subsurface irrigation as well as provide improved drainage. The owned land base and the existing machinery complement will be treated as fixed resources. Decision variables will include farm size (expandable through leased acreage), crop rotation, and other cultural practices. The model will incorporate constraints on capital, labor, and machinery capacity which are functions of both weather and drainage system during several planting and harvesting periods.

In order to understand the impact of water quality guidelines imposed on the farm firm, the base model will be modified to incorporate externally imposed constraints (pollution limits) on nitrate and phosphorus discharge. Previous studies have demonstrated that subirrigation systems have the potential to reduce the level of nutrient discharge from subsurface drains (Wright et al. 1992). In order to meet water quality guidelines, farms with conventional subsurface drainage systems will need to make greater changes in the overall organization of their farming system (e.g., reduced fertility rates, change of rotation, and/or adoption of other pollution abatement practices) than will a similar farm with subirrigation. Such alterations may significantly impact profitability.

The linear programming model will be constructed in such a way as to allow measurement of the sensitivity of the crop production activities in the optimal solution to prices of key resources, prices of commodities, and restrictions on labor or capital availability. Standard linear programming output provides estimates of the marginal value of additional resources as well as an indication of the amount by which profitability of competing activities must change before those activities would enter the optimal farm plan.

Objective 3: Develop a technical design and management guide for subirrigated agricultural production and constructed wetland-reservoir systems, and conduct an applications and design workshop to teach agricultural producers and consultants how to use water table management for environmental and economic benefit.

Technology transfer is a major component of both the existing demonstration project and the proposed project, using tri-state (Ohio, Indiana and Michigan) water management conferences and field days to teach farmers, technical and regulatory agency personnel, and non-agricultural citizens the benefits of interfacing wetlands with modern agricultural production. Research/demonstration results will be the basis for management guide development, with a primary focus on environmental and economic benefits of water table management and constructed wetlands, site identification, water supply, engineering design, construction, and system operation and management. All aspects of the existing demonstration project and proposed project will feed into Dr. Brown's educational activities conducted cooperatively by Ohio State University Extension, the demonstration project and its cooperators and technical advisors, and the Overholt Drainage Education and Research Program at The Ohio State University.

The state-of-the-art knowledge of water table management and associated constructed wetlands technologies will be developed into a comprehensive technical and educational guide on the design, operation and management of subirrigation systems that enhance water quality and sustain productivity. Research from across the Cornbelt, Great Lakes, and southeast regions of the U.S., and from Canada will be incorporated into this effort. Computer simulation models (i.e., DRAINMOD, ADAPT), and the subirrigation evaluation/design model SI-DESIGN (Belcher et al. 1993) will be used in the analysis. The results of the analyses performed to address Objectives 1 and 2 will be incorporated into this effort. Dr. Brown will conduct a series of one- to two-day planning sessions to outline the content and production schedule for the guide. The guide content will be produced by the end of year two of the project.

Field demonstrations of research is an excellent mechanism through which agricultural producers can be educated. This technology transfer technique actually incorporates complex research systems into field teaching laboratories. Field demonstration days will be organized and conducted at selected demonstration sites each year of the proposed project. Field demonstration days will be conducted in a cooperative effort by the Maumee Valley RC&D, Ohio State University Extension, and Drs. Brown and Fausey. These field demonstration days will be advertised in the Great Lakes Region. Field day participants will witness field-scale and plot-scale subirrigation, constructed wetlands on prior-converted cropland, be exposed to the operational requirements for successful subirrigation and management of a constructed wetland-reservoir, and be presented with data that supports the economic and water quality benefits of water table management by subirrigation integrated with constructed wetland-reservoirs.

The project team will conduct one regional workshop in year two of the proposed project. This will be an multi-disciplinary, interagency effort, primarily targeting agricultural producers. However, persons who provide agricultural water management services to producers will be targeted as a secondary audience (technical agency personnel, soil and water conservation contractors, consultants, etc.).

Progress report:

Wetland-Reservoir-Subirrigation Systems (WRSIS) have the potential both to improve downstream water quality by reducing discharge to streams, to provide wildlife habitat, to increase wetland acres and vegetation, and to provide a reliable supply of subirrigation water for sustained crop production. In a WRSIS, a wetland is constructed to receive subsurface drainage and runoff from adjacent cropland. The cropland is subirrigated by a water supply reservoir which is also linked to the constructed wetland. The wetland, reservoir and subirrigated cropland are integrated to recycle runoff and drainage waters.

Prior to WRRI funding, three constructed wetlands were designed, constructed, and linked with water supply reservoirs for corn and soybean production systems using subirrigation. All three systems, located in the Ohio portion of the Maumee River Basin, were operational in the 1997 and 1998 growing seasons, and provided yield data. The wetlands were constructed on prior-converted cropland (soils dominantly silty clay) to receive drainage from adjacent cropland, resulting potentially in zero-discharge from cropland directly to streams, except during extreme precipitation events. Agricultural runoff and subsurface drainage recharge the wetland seasonally, and the reservoir serves as a supplemental water supply source for subirrigating corn and soybean. The constructed wetlands, primarily designed to serve as runoff and drainage collection and detention components, have developed wetland vegetation. A comprehensive, baseline wetland vegetation survey was undertaken and completed in 1998.

Non-replicated yield data, averaged over four varieties of both corn and soybean, for 1996 (first year of study) from the Fulton County site indicated a yield increase for both corn and soybean of approximately 50% for subirrigated versus conventionally drained cropland. The 1996 growing season had normal-to-below normal rainfall. Crop seasons in 1997 and 1998 had normal to above normal rainfall. Yield data from 1997 and 1998 indicated a slight increase in yields from the subirrigated systems over the conventional drainage system. These data suggest that the system benefited from the more intensive drainage spacing with the subirrigated system compared to conventional drainage. The growing season had above normal precipitation, and a fairly uniform rainfall distribution.

A comprehensive monitoring system has been designed for the Defiance County site, and is now being completed. We are now able to collect a large variety of data useful for hydrologists, biologists, wetland ecologists, modelers and decision support system designers, engineers, and natural resources conservationists.

A summary of individual subprojects within the overall research scope follows.

Monitoring System for Water Quality and Quantity, and Ecological Parameters at the DARA Wetland-Reservoir Subirrigation System Site. At the Defiance Agricultural Research Association (DARA) site in Defiance, Ohio, an intensive monitoring program has been implemented in order to monitor and analyze the performance of the system. Instrumentation is being installed to measure system parameters necessary to fully evaluate the benefits, operation and management, and economics of the system and its components. Hydrological, agricultural, environmental, and ecological focus areas include: determination of system water balance; water routing for water conveyance, storage and water supply; subirrigation water requirements for corn and soybean production; operation and management of system components; farm-level economics; sediment routing and trapping; nutrient and pesticide fate and transport; plant community development and diversity, wetland vegetation, and vegetative habitat for wildlife; macro-invertebrate community development; net water, sediment, nutrient, and pesticide losses off-site. The ecological impact of the system is also being analyzed through the monitoring of the diversity of the vegetative growth in and around the wetland and the monitoring of aquatic macro-invertebrates within the wetland.

Water Column Sampling System for the Constructed Wetland and Water Supply Reservoir at the DARA WRSIS Site. In the WRSIS system, the wetland, reservoir and subirrigated cropland are integrated to collect and recycle runoff and drainage waters from cropland. Three systems have been developed, and the DARA site has been instrumented with a water column water sampling system to evaluate water quality parameters in the wetland and reservoir. A prototype sampling system was designed by our undergraduate engineering students as a design exercise.

Modeling of Water Routing in a Wetland-Reservoir-Subirrigation System Using SIMULINK. WRSIS have the potential both to improve downstream water quality by reducing discharge to streams and to provide a reliable supply of subirrigation water. In order to help evaluate the design, management, and performance of such systems, a model has being developed to simulate the routing of water between the system's components and to model the water balance within each of the components. This work is being done using SIMULINK, a software package which uses block diagrams to define dynamic systems. In the model, an entire library of blocks representing each of the different components of the system (i.e., wetland, subirrigated field, pump station, reservoir, etc.) can be developed. Each of these blocks actually represents a sub-system of blocks that model the dynamic behavior of that component. The system component blocks can be linked to model a wide range of system configurations for WRSIS sites. The model can also be used to analyze a variety of different management strategies. The model is being calibrated and tested at the DARA site, and management strategies will be tested on the other two sites. Future development will focus on automatic system operation and optimization, and real-world implementation.

Modeling of Water and Sediment Routing in a Wetland-Reservoir-Subirrigation System Using the WEPP Watershed Model. In addition to the modeling work above, we are currently modifying and evaluating the WEPP Watershed model, which contains a hydrologic elements, impoundments, and routing routines for water and sediment. We are modifying the model to incorporate a more robust water table management component to handle subirrigated and drainage controlled landscapes. We are now completing evaluation of the modified subsurface drainage component against data from a previous northwest Ohio study, and are now beginning the work with the modified subirrigation and controlled drainage routines.

Farm Level Economics and Capital Costs Analysis of Three Wetland-Reservoir Subirrigation System Sites in Northwestern Ohio. The construction all three sites was completed in 1996 and 1997. Construction and all other capital costs were documented and analyzed. A survey of drainage and land improvement contractors was implemented to ascertain local construction cost information (average costs and ranges) for different system components (design, site preparation, wetland, reservoir, subirrigation, pumping plant, drainage, waterways, etc.) to compare to the costs data for these three systems. Yield data from the first two years of this project and from subirrigation research plots from other locations in Ohio and Michigan, will be used to analyze the benefits of these systems for improved and sustained crop production. Yield data from several long-term crop yield studies with conventional subsurface drainage are being analyzed for use in comparisons with the WRSIS yield results. The overall analysis of these costs will be used to provide to farmers information for use in evaluating their application of the technology.

Several professional papers were completed and presented in FY 1998. The economic analysis paper has been accepted for publication. The overall project has been summarized in a variety of outreach publications.

The project enjoys great interdisciplinary, multi-agency, and stakeholder participation. The overall project is a cooperative team effort between the Maumee Valley RC&D (MVRC&D), USDA-Natural Resources Conservation Service (NRCS), USDA-Agricultural Research Service (ARS) Soil Drainage Research Unit, The Ohio State University (OSU), Michigan State University (MSU), Heidelberg College (HC), Soil and Water Conservation Districts (SWCD), farm cooperators and county commissioners, Ohio and Michigan Land Improvement Contractors (O&MLICA), Drainage Products Industry (ADS, Hancor, Haviland, Baughman), ODNR Division of Wildlife (SW), USF&WS, USACOE, and other local and state agencies and organizations.

The overall project funding is provided, in part, by USEPA GLNPO; Lake Erie Protection Fund; OARDC and OSU Extension; Ohio Sea Grant College Program; USGS Water Resources Competitive Grants Program; Water Resources Center, The Ohio State University; USDA-ARS Soil Drainage Research Unit; USDA-CSREES Hatch Proj. 965; Overholt Drainage Education and Research Program, Dept. Food, Agric., and Biol. Engr., The Ohio State University; and the cooperating landowners, agencies and organizations. A second WRRI funded sub-project to the overall WRSIS project was initiated in FY 1999 (see elsewhere in this report).

This innovative, ecologically sound crop production system will recycle runoff and drainage waters, reduce runoff, sediment, and agricultural chemical discharges to streams, improve water quality, increase wildlife habitat, increase wetland acres, and enhance farm profitability. The demonstration project team (farmers, state and federal agency personnel, university faculty) will provide high level input to proposed research and help evaluate application of results to users. Integrated research and demonstration efforts will produce a management guide with focus on environmental and economic benefits, site identification, water supply, engineering design, construction, and system operation and management.

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Brown, L.C. (Editor). 1998. Drainage in the 21st Century: Food Production and the Environment. Proceedings of the 7th International Drainage Symposium. Vol. 7:02-98, ASAE: St. Joseph, MI. 738 pp.

Brown, L.C., B.J. Czartoski, N.R. Fausey, and H.W. Belcher. 1998. Integrating constructed wetlands, water supply reservoirs, and subirrigation into a high yield potential corn and soybean production system. In: Proceedings of the 7th International Drainage Symposium. Vol. 7:02-98, ASAE: St. Joseph, MI. Pp. 523-529.

Brown, L.C., B.M. Schmitz, M.T. Batte, C. Eppley, G.O. Schwab, R.C. Reeder, D.J. Eckert. 1998. Historic drainage, tillage, crop rotation, and yield studies on clay soils in Ohio. In: Proceedings of the 7th International Drainage Symposium. Vol. 7:02-98, ASAE: St. Joseph, MI. Pp. 456-464.

Other Publications

Hothem, J.A. and L.C. Brown. 1998. Modeling of water routing in a wetland-reservoir-subirrigation system using SIMULINK. Paper No. 982096. Presented at 1998 ASAE Annual Meeting. ASAE: St. Joseph, MI. 11 pp.

Myers, M., Miller, B.A., Jacobs, M., N'jie, N.M., Soboyejo, A., Brown, L.C. 1998. Water column sampling system for the constructed wetland and water supply reservoir at the DARA WRSIS site. Paper No. 982094. Presented at 1998 ASAE Annual Meeting. ASAE: St. Joseph, MI. 10 pp.

Oztekin, T., Hothem, J.A., N'jie, N.M., Luckeydoo, L., Mills, G., Brown, L.C., Fausey, N.R., Czartoski, B.J. 1998. Monitoring system for water quality and quantity, and ecological parameters at the DARA wetland-reservoir subirrigation system site. Paper No. 982110. Presented at 1998 ASAE Annual Meeting. ASAE: St. Joseph, MI. 7 pp.

Richards, S.T., Batte, M.T., Brown, L.C., Czartoski, B.J., Fausey, N.R., Belcher, H.W. 1998. Farm level economics and capital costs analysis of three wetland reservoir subirrigation system sites in Northwestern Ohio. Paper No. 982020. Presented at 1998 ASAE Annual Meeting. ASAE: St. Joseph, MI. 16 pp.

Tornes, L., B.C. Atherton, L.C. Brown, R.M. Gehring, B. Slater, J.R. Steiger, T.L. Zimmerman, N.R. Fausey, G.S. Hall and M. Debrock. 1998. Soil property database for design, construction, operation and management of agricultural water management systems for irrigation, constructed wetlands, drainage, and environmental considerations. Paper No. 982109. Presented at 1998 ASAE Annual Meeting. ASAE: St. Joseph, MI. 16 pp.

Zucker, L.A. and L.C. Brown. (Eds.). 1998. Agricultural Drainage: Water Quality Impacts and Subsurface Drainage Studies in the Midwest. Ohio State University Extension, Bulletin 871. The Ohio State University. 40 pp.

Technical Publications

Subirrigation Design, Operation and Management. Designing Agricultural Systems to Balance Production and Environmental Objectives. Miscellaneous Bulletin OAWMGWP No. 1-3/1999. Food, Agricultural, and Biological Engineering Department, The Ohio State University.

Subsurface Drainage Design, Operation and Management. Designing Agricultural Systems to Balance Production and Environmental Objectives. Miscellaneous Bulletin OAWMGWP No. 2-3/1999. Food, Agricultural, and Biological Engineering Department, The Ohio State University.

Agricultural Constructed Wetlands, and Wetland-Reservoir Subirrigation Systems. Designing Agricultural Systems to Balance Production and Environmental Objectives. Miscellaneous Bulletin OAWMGWP No. 3/3-1999. Food, Agricultural, and Biological Engineering Department, The Ohio State University.

Soil Properties Important for Drainage. Designing Agricultural Systems to Balance Production and Environmental Objectives. Miscellaneous Bulletin OAWMGWP No. 4/3-1999. Food, Agricultural, and Biological Engineering Department, The Ohio State University.

Soil Properties Important for Irrigation. Designing Agricultural Systems to Balance Production and Environmental Objectives. Miscellaneous Bulletin OAWMGWP No. 5/3-1999. Food, Agricultural, and Biological Engineering Department, The Ohio State University.

Subsurface Drainage Spacing and Depth Analysis for Reference Soils in Ohio. Designing Agricultural Systems to Balance Production and Environmental Objectives. Miscellaneous Bulletin OAWMGWP No. 6/3-1999. Food, Agricultural, and Biological Engineering Department, The Ohio State University.

Presentations Scheduled:

L.M. Luckeydoo. ____. Vegetation Surveys for Constructed Wetlands of the Wetland Reservoir Subirrigation Systems. Abstract submitted to OAS.

L.C. Brown, N.R. Fausey, B.J. Czartoski, H.W. Belcher, J.A. Hothem, N.M. N'Jie, T. Oztekin, L. Luckeydoo, M.T. Batte, C. Davis, Fred, Marge, and Bill Shininger, P. Chester, B. Clevenger, L. Davis, P. Andre, D. Sutton. ____. Marketing Wetlands for Profit. Oral presentation, poster, and summary paper accepted for SWCS annual meeting.

L.C. Brown, N.R. Fausey, A.D. Ward, L.A. Zucker. ____. The Midwest Water Management ASEQ: Agricultural Drainage and Nitrate. (presentation and extended abstract for The Third National Workshop on Constructed Wetlands/BMPs for Nutrient Reduction and Coastal Water Protection, June 9-12, 1999, New Orleans, Louisiana).

Information Transfer Program:

In addition to the International professional meeting papers listed elsewhere, other presentations were made in 1998 on the overall project scope, demonstration, monitoring and research plans, and others are scheduled for 1999:

1998 National Land Improvement Contractors meeting in Nashville, TN on February 18-19, 1998;

Ohio Sea Grant Program personnel at Ohio State University April 7;

Water Seminar Luncheon sponsored by the Water Resources Center at Ohio State University on April 14, 1998, A novel approach to incorporating constructed wetlands into an economical and environmentally friendly agricultural production system in the Maumee River Basin, Columbus;

Annual Northwest Ohio Drainage Expo, Water Table Management and WRSIS Impacts on Water Quality, Defiance County;

Valuing Lost Sediments and Nutrients from Production Systems In-Service, Environmental Effluents, Measuring NPS Pollution, Modeling Effluents from Agriculture, Columbus;

Regional Agronomy Meetings, Northwest District, Water Table Management and WRSIS; Shininger Farm Field Day, Fulton County,
Wetland-Reservoir Subirrigation Systems;Soil Erosion and Sediment Control Opportunities for the Great Lakes Basin Conference, Water Table Management and WRSIS Impacts on Water Quality, Toledo, Poster;

Woodburn, IN, Soil and Water Training and Media Day, Conservation Tillage Center of Excellence, SWCD/Purdue Extension, Drainage Economics and Water Quality, Allen County;

Amana, IA, Watershed Heroes Conference, American Farm Bureau Federation, Drainage and Nitrogen Management;

Ft. Collins, CO, ARS National Program on Water Quality and Management, USDA-ARS National Program Staff, Drainage Management;

Washington, DC, Agricultural Research and Education, A University Science Exhibition on Capital Hill, Innovative Agricultural Water Management: Wetlands and Modern Agriculture, Poster Exhibition;

Lincoln, NE, Biological Systems Engineering Departmental Seminar, Agricultural Water Management Systems: An Ohio Example Using Water Table Management and Wetlands;

A one-day technical session on the system was presented at the 1998 Overholt Drainage School at Ohio State University on March 20, with 35 contractors, consultants, engineers, extension agents, and soil and water conservation technical agency personnel attending.

In March of 1999, the Overholt Drainage School will conduct a weeklong short course on the following topics: Design, construction, operation and management of Subirrigation, Subsurface drainage, Controlled drainage, and Wetland-Reservoir Subirrigation Systems. Over 80 contractors, engineers, resources agency personnel are expected to attend portions of the short course. Field site visits will be made to the Fulton County site.

A poster presentation titled "Innovative agricultural water management systems create a win-win for food production and environmental quality objectives" was presented at How Agricultural Science Research Serves the Nation: A University Exhibition and Reception on Capitol Hill, May 19, 1998, and a two-page handout was developed.

Training Accomplishments:
Student Support:

Students

Undergraduate	5 (part-time; partial match)
Masters	2 (federal $ and partial match)
Non-Thesis Masters	1 (federal $ and partial match)
Ph.D.	2 (federal $ and partial match)
Post Ph.D.	0

Disciplines

Undergraduate	4 - Food, Agric., and Biol. Engr
	1 - Environmental Sciences
Masters	1 - Food, Agric., and Biol. Engr.
	1 - Environmental Sciences
Non-Thesis Masters	1 – Agricultural, Developmental, and Environmental Economics
Ph.D.	1 - Food, Agric., and Biol. Engr.
	1 - Environmental Sciences
Post Ph.D.	0

Synopsis

Project Number: C-04

Start. 09/97
End. 09/99

Title: **Degradation of Groundwater Quality from Pumping-Induced Surface-Water Infiltration: Bacterial Contamination**

Investigators: Jonathan Levy, Miami University, Oxford, OH 45056
Robert H. Findlay, Miami University, Oxford, OH 45056
Kerang Sun, Miami University, Oxford, OH 45056
Heidi L. Schran, Miami University, Oxford, OH 45056
Amy Lustig, Miami University, Oxford, OH 45056

Congressional District: Ohio 8th

Focus Category: ECL, G&G, GW, HYDGEO, HYDROL, MOD, NPP, ST, WQL, WS

Descriptors: Autochthonous-allochthonous microbial interactions, Bacterial transport, Groundwater quality modeling, Surface-groundwater relationships.

Problem and research objectives: Drinking water pumped from shallow glacial-fluvial aquifers may be contaminated with fecal coliform bacteria derived from nearby polluted surface waters. Municipal wells located adjacent to polluted streams and rivers are especially susceptible to contamination. Due to downward hydraulic gradients induced by pumping, contaminated surface water may be drawn into the underlying aquifer and move towards drinking-water wells. Under US EPA guidelines, wells less than 50 ft from surface water are considered under the direct influence of surface water. From a regulatory standpoint, the Ohio EPA mandates that such groundwater be treated as if it were surface water and therefore requires the water to be treated with techniques for coagulation/flocculation, settling, filtration and disinfection. Upgrading typical groundwater treatment to include these techniques can be quite costly and in many circumstances prohibitive, resulting in well abandonment and the costly search for new water supplies. Studies in bacterial transport through groundwater suggest that the 50-ft criterion will not be cautious enough in some settings and too cautious in others. Adequate guidelines for appropriate separation distances need to be developed and should be based on our best ability to predict bacterial transport in a variety of hydrogeologic settings. Private wells are also susceptible to bacterial contamination. In a recent study of well-water quality in Iowa, 78% of wells in a volunteer sampling program were found to test positive for total coliform bacteria. The majority of these wells were shallow (67%) and were located > 100 ft from the closest active barnyard/feedlot and > 50 ft from a septic system (92%). Clearly, both rural populations obtaining drinking water from private wells and municipal populations obtaining drinking water from aquifers adjacent to polluted surface waters are at risk of waterborne disease. Our objective in this study is to help develop the ability to predict allochthonous (invasive, nonindigenous) bacterial transport through groundwater aquifers, allowing greater protection of groundwater that is to be used as a drinking-water source.

Our overall research objective is to advance the ability to predict allochthonous bacterial transport and fate through groundwater aquifers. We note two main deficiencies with current models. The first is that the complexity of current models prohibits their use as regulatory tools for determining appropriate separation distances between bacterial sources and drinking-water wells. While the processes have been theoretically described, little work has been done toward their quantification or their relationship to real-world aquifers. Second, previous studies grounded in real complex systems have paid little attention to the impact of the interactions between allochthonous and autochthonous microbial communities of groundwater. Failure to predict retardation and immobilization or decay of allochthonous species accurately may be due to a failure to incorporate microbial interactions into existing models. With this research we directly address these two deficiencies. We approach the problem with a series of testable hypotheses, which we are investigating using a combination of laboratory column experiments under controlled and variable conditions and statistical and computer modeling. We also are initiating field studies to collect real-world data and test new models.

Hypothesis 1: The autochthonous microbial community significantly affects the transport of allochthonous bacteria through groundwater. The effects of autochthonous microbial communities on pathogenic bacterial transport result from predation and other ammensal or commensal interactions. These interactions result in either apparent decay or retardation of the allochthonous species. Autochthonous bacteria are part of a complex biofilm on aquifer sediments that also includes non-living organic matter. We wish to differentiate the effects of the organic matter from the living indigenous microbial community and we hypothesize that the interactions with autochthonous bacteria are significant apart from the effects of the nonliving biofilm component. Our experimental transport columns will therefore be treated to represent aquifer material with and without a viable autochthonous community and with and without any biofilm present. Apparent decay and retardation rates will be compared between treatments. We predict that interactions with the autochthonous community will result in an apparent difference in bacterial transport velocity compared to a conservative tracer and a decrease in the total number of allochthonous bacteria exiting the columns.

Hypothesis 2: A useful predictive model can be developed for allochthonous bacterial transport through aquifer sediments. In Year 2, we will build on the data generated through testing Hypothesis 1. Our goal is to be able to predict allochthonous bacterial transport and fate in groundwater given a set of biotic and abiotic aquifer characteristics. Developing this capability is a two-step process. In the first step, we will conduct dozens of column experiments in addition to those run for testing of Hypothesis 1, and we will measure the biotic and abiotic aquifer characteristics that influence bacterial transport and fate. The columns will comprise sediment taken from a variety of hydrogeological settings and will be run under controlled temperature conditions. For each column we will generate a bacterial breakthrough and dilution curve. In the second step, we will use a one-dimensional advection-dispersion-reaction model that simulates results comparable to the experimental curves. Each column will have its own associated model parameter values. We will use multiple regression analysis to relate the calibrated transport-model parameter values to the aquifer characteristics that are most likely to control bacterial transport. The end result is a model which uses aquifer characteristics to predict bacterial transport and fate in a wide variety of settings. A strength of such a model is that it can incorporate the spatial variability and uncertainty of the aquifer characteristics to quantify the uncertainty associated with the final transport-model predictions.

Hypothesis 3: The bacterial-transport model developed in the laboratory will accurately predict bacterial transport in the field. We will begin development of a permanent field-test site. We have access to an abandoned City of Oxford, Ohio well that has sporadically tested positive for total coliform bacteria. The well is under the direct influence of Four Mile Creek. We will use the well to induce a vertical hydraulic gradient and use that gradient to perform conservative tracer tests and observe bacterial transport and fate along flow paths from the creek toward the well. A combination of single piezometers, nested piezometers and multilevel sampling devices will be used to determine the horizontal and vertical concentrations of chemical and microbiological components of groundwater. Biotic and abiotic aquifer characteristics will be determined from sediments recovered during piezometer placement. We will predict bacterial fate and transport using our model and the predictions will be compared to the observed bacterial concentrations.

Methodology:

Hypothesis 1: The autochthonous microbial community significantly affects the transport of allochthonous bacteria through groundwater.

Undisturbed groundwater sediments are collected using a drilling rig and a split-spoon sampler. The sediment is collected into a polycarbonate, split-spoon liner from which a 10-cm section is chosen. The ends of the sediment sample are sampled three times for phospholipid fatty acid (PLFA) analysis and the remaining sample is incorporated into a flow-through column apparatus. The sediment core is kept saturated throughout this process. A flow rate of about 12-ml/hr is then established through the column to simulate local natural groundwater flow conditions. Bacterial and bromide breakthrough experiments are run by pulling a pulse of either bacterial suspension in natural groundwater or bromide solution through the column using a peristaltic pump. For the bacterial-breakthrough experiment, the column effluent is sampled at six-minute intervals using an autosampler, and the samples are analyzed with membrane filtration techniques. For the bromide breakthrough experiment, the effluent is analyzed using an ion-specific electrode or samples are collected for analysis by high-performance liquid chromatography (HPLC).

If possible, data from the breakthrough experiments are reproduced with a computer analytical model of contaminant transport. Matching the model predictions to the bromide experiment data, velocity and dispersivity are determined. Knowing the pumping rate and velocity allows calculation of an effective porosity. Knowing the effective porosity allows determination of groundwater flow velocity in the bacterial breakthrough experiment. Using the computed velocity and the dispersivity calculated from the fitted dispersion coefficient from the bromide experiment, bacterial-reaction coefficients are determined by fitting model results to the bacterial-breakthrough data. To test Hypothesis 1, this process is repeated with replicates on intact sediment (Treatment 1) and on sediment after killing off the autochthonous microbial community (Treatment 2). The reaction coefficients obtained from each treatment are then compared using analysis of variance techniques.

Hypothesis 2: A useful predictive model can be developed for allochthonous bacterial transport through aquifer sediments. We are attempting to investigate the factors that affect the transport of allochthonous bacteria through groundwater sediments. These factors will be quantifiable aquifer system characteristics. The primary factors affecting allochthonous bacterial transport include hydraulic conductivity, effective porosity, mineralogy, organic matter content and grain-size distribution of aquifer material. We will run bacterial and bromide breakthrough experiments on sediment cores collected from a variety of locations. The procedures for running the experiments, quantifying the autochthonous microbial community and fitting the breakthrough curves, will be the same as described for Hypothesis 1. Upon completion of the flow-through experiments, the column sediments and/or sediments from the original cores close to the column sediments will undergo abiotic characterization. We will then perform multiple linear regression analysis to relate calibrated transport model parameter values to aquifer characteristics. Various regression models will be explored for good fits. Forward selection and backward elimination procedures will be employed. Correlation between possible independent variables will be investigated. Only those variables with t-ratios > approximately 2.0 will be included in the final regression models. Equation robustness to changes in variable inclusion will be considered. To improve fits, transformations on the regression variables will be explored including logarithmic, square root and reciprocal transformations. Multiple linear regression models will be selected on the basis of the highest R^2 value with statistically significant variables. Plots of standardized residuals versus the fitted dependent variable value will be examined to judge the model fit.

Hypothesis 3: The bacterial-transport model developed in the laboratory will accurately predict bacterial transport in the field. We have developed a field site in the Four Mile Creek basin near Oxford, Ohio for eventual field-testing of our model. The site will use a drinking-water well formerly operated by the City of Oxford. The well is set in a 12-m layer of heterogeneous, permeable, glacial outwash deposits. A dense, clayey glacial till underlies the outwash, confining groundwater flow. The pumping well is a Ranney® collector with horizontal, screened collector arms, installed at depth and extending radially out from a vertical caisson. Water is drawn from the adjacent Four Mile Creek. Water from this well has sporadically tested positive for fecal coliform bacteria. The field area near the Ranney collector provides an excellent site for investigation of bacterial transport through groundwater. We will use a single arm of the

Ranney collector to induce a hydraulic gradient and use that gradient, to perform conservative tracer tests and observe bacterial transport and fate along flow paths from the creek toward the pumping well. Field data will be used to test the modeling approaches presented.

A combination of single and nested piezometers and multilevel sampling devices have been used to determine hydraulic conductivities and will be used to determine the horizontal and vertical concentrations of chemical and microbiological components of groundwater. Hydraulic conductivities are investigated using an aquifer pumping test, piezometer slug tests and laboratory permeameters.

Forced-gradient tracer tests will be performed using a bromide solution. Approximately 100 liters of groundwater with a bromide concentration of 180 mg/l will be injected into 3 piezometers placed directly below the Four Mile Creek bed. Bromide will be used as a conservative tracer because of its low background concentration in the aquifer. The injection wells will be located so that they are directly upgradient of the multilevel sampling array under pumping-induced gradients. Based on our experience with this aquifer, expected travel time from the creek to the radial arm is one to two days. Samples will be collected and brought to the laboratory for bromide analysis with the HPLC. Moment analysis on bromide concentrations will be used to determine the movement of the center of mass for velocity determination and the change in concentration variance for determination of apparent longitudinal dispersivity. Using these data we will predict allochthonous bacterial distribution within the flow path. Concurrent with the bromide tracer studies the distribution of allochthonous bacteria within the flow field will be determined and compared with model predictions.

Principal findings and significance:

Hypotheses 1 and 2

Our initial column apparatus was designed to incorporate 3.4-cm ID columns. The design allows for natural sediments to be used in a controlled laboratory setting without disturbing the physical structure of the aquifer sediments or the autochthonous microbial community. These features are essential for investigating the role of the indigenous microbial community on the transport of invasive bacteria. Natural sediment cores were taken from the local groundwater aquifer and 10-cm sections of these cores were chosen and incorporated into the column apparatus. Bromide and bacterial flow-through experiments were performed on those columns to test our hypothesis that the indigenous microbial community has interactions that significantly affect the survival and retardation rates of invasive pathogens in groundwater. The column apparatus, along with a technique to kill the indigenous microbial community, allowed us to set up two treatments for our experimental design. Results from the two treatments were compared and the effect of indigenous microbial community on invasive bacterial transport was studied.

A 10-ml, 200 µg/ml bromide slug, prepared from local groundwater, was used in the experiments. A bromide ion-specific electrode (ISE), connected in-line to the effluent tubing, was used to measure the bromide concentrations in the effluent. All the breakthrough curves obtained from bromide experiments were asymmetrical and exhibited long tailing. The cause of the skewness and tailing for non-reactive tracers such as bromide is probably the existence of immobile or stagnant water regions and solute exchange between the mobile and immobile regions. A physical non-equilibrium, two-region model that explicitly accounts for the mass exchange between the mobile and immobile regions was therefore applied to better simulate the experiment data. CXTFIT2.0 software (Toride et al., 1995) was used to simulate the breakthrough experimental data. This program can be used to estimate transport parameters in both the equilibrium mode and the non-equilibrium, two-region mode. Model parameter values are estimated by fitting the observed data with a simulated curve. The simulated and observed curves are matched by minimizing the sum of the squared differences using a nonlinear least-squares inversion method. Figure 1 shows the bromide breakthrough data for the 9-11-98 core modeled with both the equilibrium model and the two-region model. The two-region model better simulates the entire curve, especially the long tail. Since the two-region model better represents the bromide breakthrough data, it was chosen for all bromide modeling. Values of effective porosity and dispersivity were calculated based on the modeling results from two-region model.

It is essential that the column apparatus be able to reproduce experimental data. The reproducibility of the bromide breakthrough experiment was tested with replicate runs on each core. All the replicate bromide runs were performed under similar conditions. However, with the pump we were using, the flow rate varied slightly among the replicate runs. Figure 2 shows the breakthrough curves of the replicate runs for the 9-11-98 core. Run 1 had a slightly higher flow rate, and therefore has a larger peak concentration than Runs 2 and 3. The two-region model was used to reproduce the experiment data; values for transport parameters are presented in Table 1. The values for effective porosity obtained from the replicate runs vary only slightly; however, fitted dispersivity values have a larger variance.

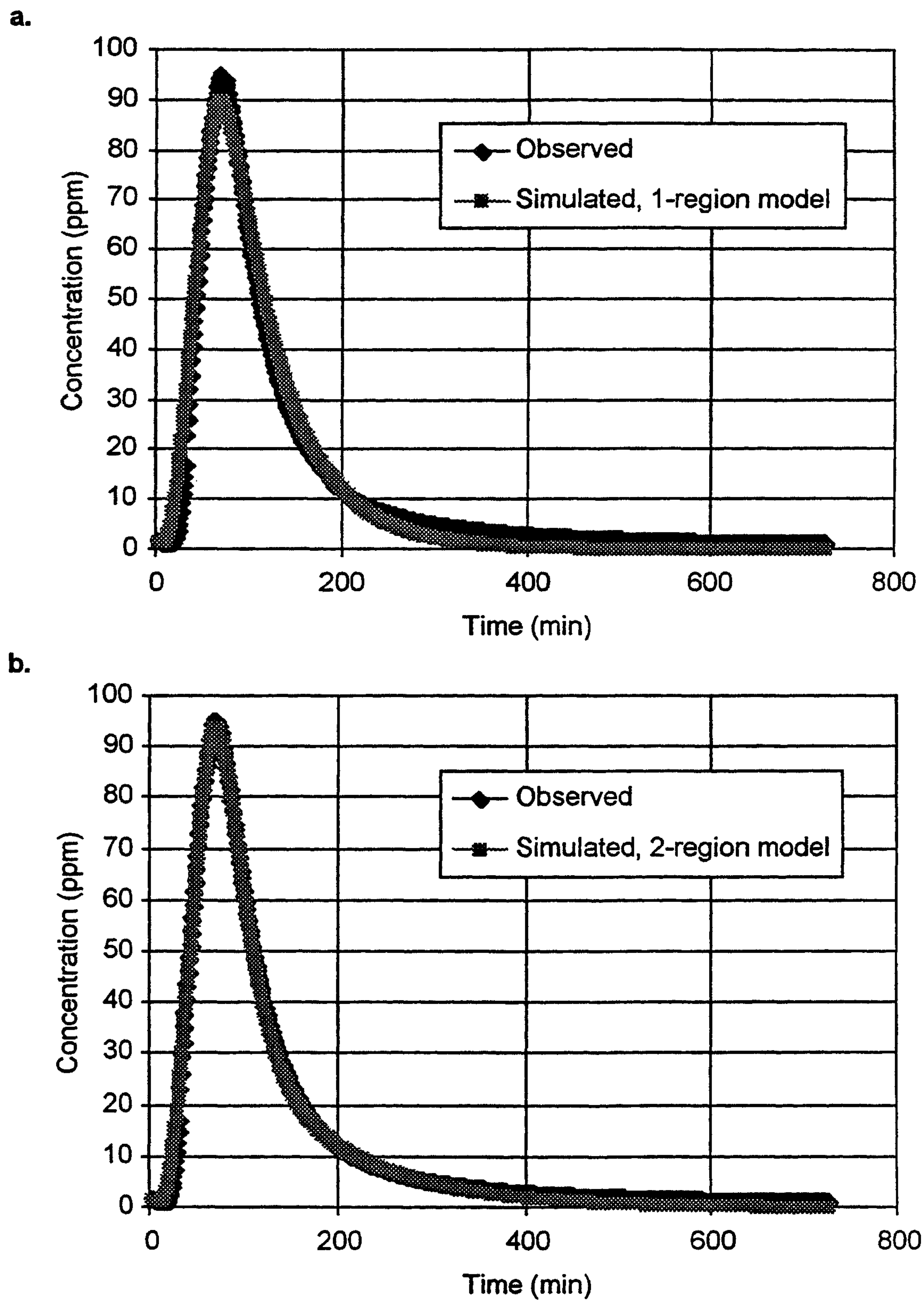


Figure 1. Bromide breakthrough data and model predictions for a) the equilibrium model and b) the physical non-equilibrium, two-region model.

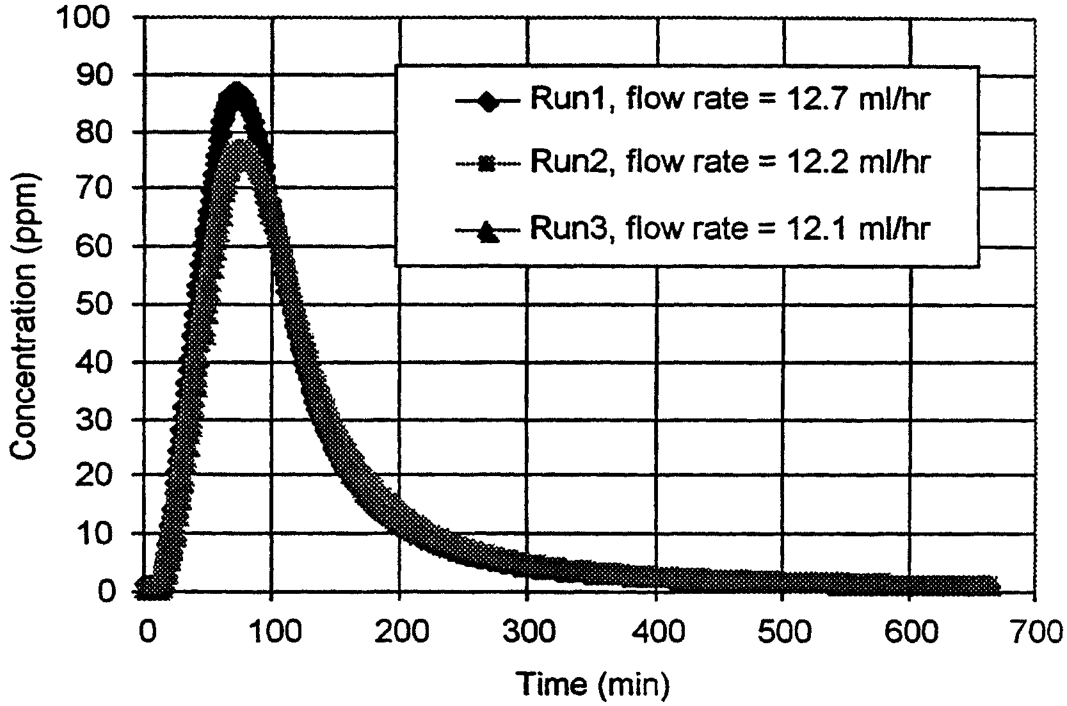


Figure 2. Breakthrough curves obtained from three duplicate runs on the same core

Table 1. Parameters of duplicate bromide runs before and after pasteurization

Pasteurization	**Run #**	**Flow rate (ml/hr)**	**C_{max}/C_0**	**C_{max} arrival time (pore volumes)**	□	**Dispersivity (cm)**
Before	1	12.7	0.436	1.13	0.14	2.98
	2	12.2	0.386	1.09	0.15	3.53
	3	12.1	0.386	1.06	0.15	2.63
After	1	13.5	0.475	1.24	0.13	1.63
	2	6.8	0.466	1.23	0.15	1.56
	3	10.6	0.428	1.14	0.15	1.89

Pasteurization was employed to kill the autochthonous microbial community. It is critical that the physical structure of the aquifer sediments is not altered by pasteurization. Bromide flow-through experiments were also used to check the effect of pasteurization on sediment physical structure. This was tested by comparing bromide breakthrough results obtained from the same core before and after pasteurization. Figure 3 shows the bromide breakthrough curves obtained from the experiments before and after pasteurization of the 9-11-98 core. Again, the difference in peak concentration is due to a slightly different flow rate. Effective porosity values obtained from the two runs are very similar (Table 1). Dispersivity values are smaller after pasteurization. Based on the effective porosity values and the similarities in the breakthrough curves, we concluded that pasteurization does not substantially affect the sediment's physical properties.

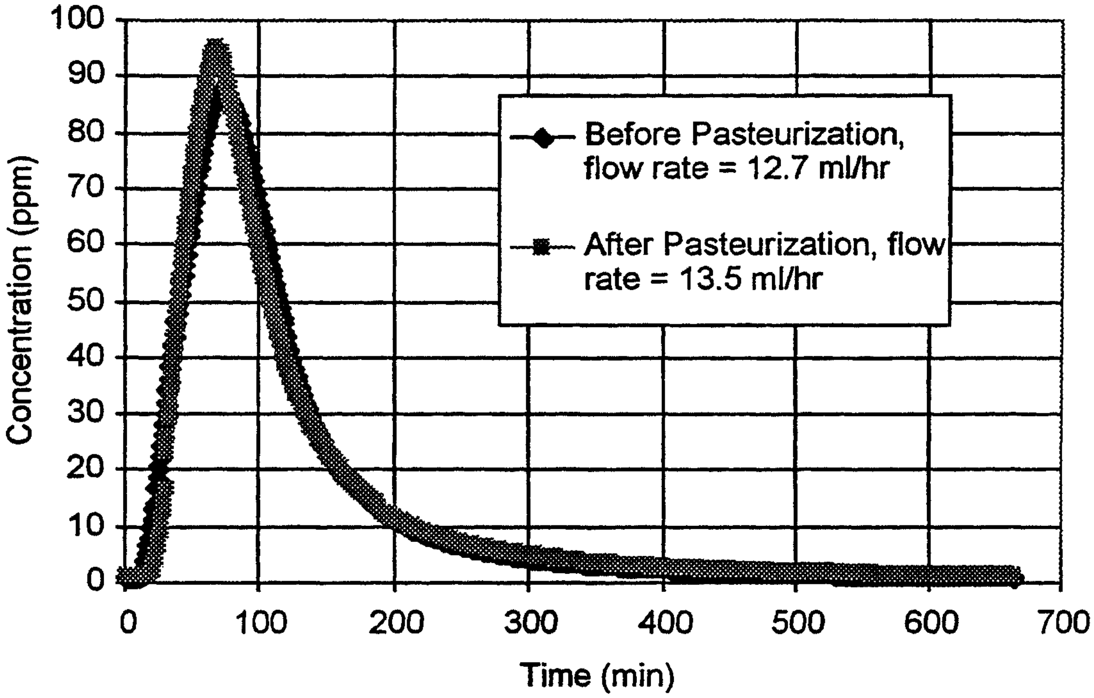


Figure 3. Bromide breakthrough curves before and after pasteurization.

To test our hypothesis that the indigenous microbial community has interactions that significantly affect the survival and retardation rates of invasive pathogens in groundwater, bacterial breakthrough results before and after pasteurization were compared. Figure 4 shows the breakthrough curves obtained from bacterial flow-through experiments before and after pasteurization for the 9-11-98 core. The two experiments were performed under similar conditions. The bacterial slug had a concentration of 10^9 CFU/mL and the slug injection period was 400 minutes for both experiments. Unlike the bromide curves, the bacterial breakthrough curves have non-classical shapes. Both curves drop quickly after reaching the peak concentrations; the decrease occurs within the slug injection period. The arrival of peak concentrations is delayed for both curves compared to a conservative tracer (bromide). The relative peak concentrations are also much lower than those of bromide. In other words, both attenuation and retardation are observed in bacterial breakthrough.

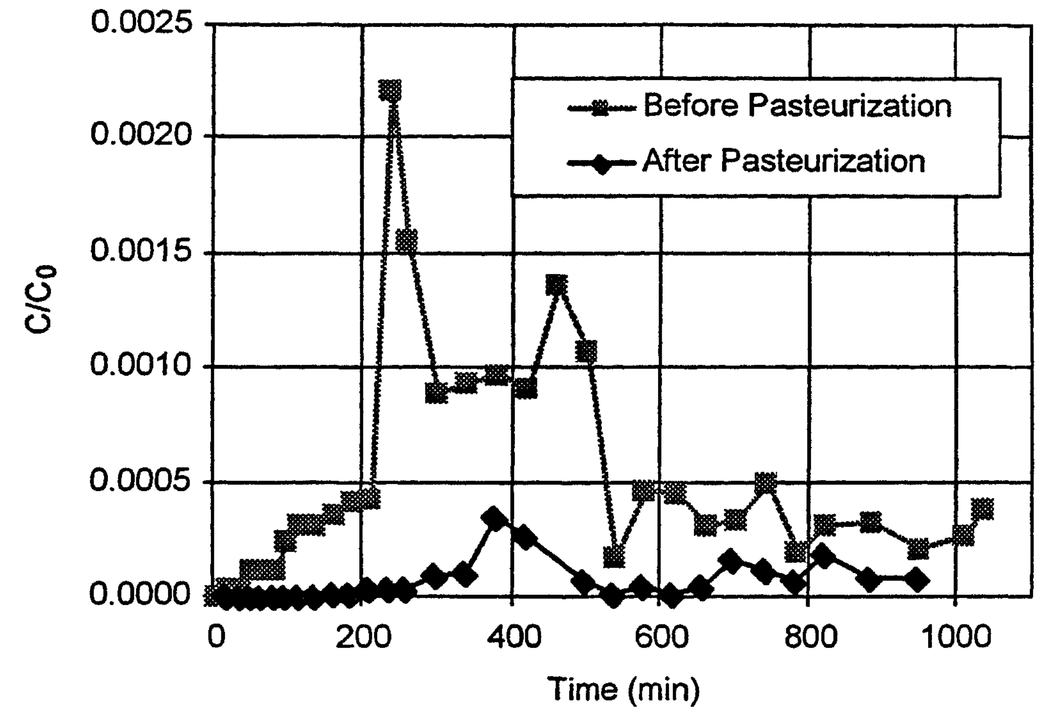


Figure 4. Comparison of bacterial breakthrough before and after pasteurization.

The non-classical shape of the breakthrough curves prohibited modeling the curves and obtaining a retardation or attenuation rate. To compare the two bacterial breakthrough curves, two alternative parameters were chosen: the relative peak concentration (C_{max}/C_0) and the arrival time (in pore volumes) of C_{max}. Both parameters changed to a great extent after pasteurization (Table 2). Based on the results of this experiment, pasteurization increases bacterial attenuation and retardation. It is possible that pasteurization may have altered the physical structure of the sediments; however, pasteurization has little effect on the bromide transport. It is, therefore, reasonable to conclude that pasteurization does not significantly affect the physical structure of natural sediments. A second explanation is that the sorption properties of the natural sediments were changed by pasteurization, which, in turn, resulted in the change of bacterial breakthrough. A third explanation is that the autochthonous bacteria may compete for reversible and/or irreversible sorption sites. Killing the autochthonous bacteria frees sorption sites, making the sites available for allochthonous bacterial sorption. This suggests that the presence and nature of the autochthonous microbial communities significantly affects the transport of allochthonous bacteria transport through groundwater. More work needs to be done to confirm the experiment results.

Table 2. Effect of pasteurization on bacterial breakthrough

Pasteurization	C_{max}/C_0	C_{max} arrival time (pore volumes)
Before	0.0022	3.8
After	0.00025	6.8

Results from new experimental setup

We have now begun to work with bigger columns. Bigger columns allow collection of more representative samples from the field. With a larger split-spoon sampler and liner we are able to include larger-sized particles and obtain more sample with less chance of sampling refusal. The experiment protocol is basically kept the same as that with the original columns, with a few changes made to improve the experiment setup. A new column apparatus was made to incorporate a 10-cm long by 6-cm diameter column rather than the previous 3.4-cm diameter column. We have also decided to inject fluids into the column bottom and flow upwards. An upward flow helps remove any air bubbles trapped in the column and, in the case of the bacterial experiment, can also minimize the effect of gravity on bacterial transport. A variable-speed, digital Masterflex L/S peristaltic pump was purchased to better maintain a constant flow rate. We also changed the bromide analysis method. The bromide ion-specific electrode (ISE) was originally used to collect bromide data. However, minor drifting of the ISE reading often occurred and we could not obtain the desired accuracy. We are now collecting samples for HPLC analysis with a Dionet DX500 chromatography system and Peaknettm software.

In order to test the new column setup, quartz sand columns were packed and both bromide and bacterial flow-through experiments were performed, collecting column effluent in a fraction collector at an 8-minute interval. Figure 5 shows the breakthrough curves obtained from two bromide flow-through experiments performed on the same sand column. The new digital pump allowed us to establish a constant flow rate of 0.6 mL/min; a slug of 6 mL of 99.68 ppm bromide solution was used. The two curves are almost identical. In addition, total mass recoveries were very close to 100%. Based on these results, the bromide breakthrough data appear highly reproducible and the new column setup works very well. For quartz sand columns, equilibrium transport of bromide can be expected. Therefore, an equilibrium model was used to simulate the experiment data. Table 3 gives the transport parameters obtained from model simulation. Again, the values for the effective porosity and dispersivity obtained from the two replicate runs are almost identical.

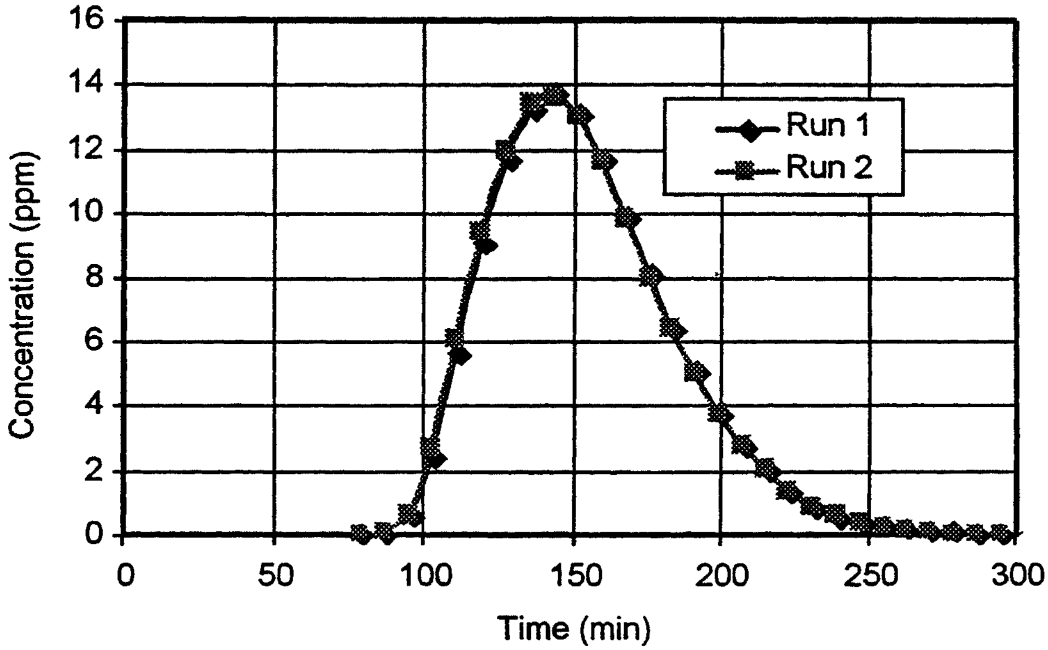


Figure 5. Two replicate bromide runs performed on the same sand column.

Table 3. Transport parameters obtained from the two bromide experiments.

	Effective Porosity	Dispersivity (cm)	Model fit R^2	Mass Recovery (%)
Run 1	0.3035	0.2154	0.9956	101.41
Run 2	0.3049	0.2117	0.9960	101.10
Difference (%)	0.46	1.74	NA	NA

A bacterial flow-through experiment was also performed on the same sand column. The slug concentration of the bacterial experiment was 1.9×10^9 CFU/mL, and the flow rate and slug duration time were the same as those of the bromide experiments. Figure 6 shows a comparison between the bacterial and bromide breakthrough curves. Even with the quartz sand column, the bacterial breakthrough curve is non-classical. Table 4 lists the breakthrough curve parameters in comparison to those of bromide experiments. Interestingly, the peak arrival of bacteria was slightly earlier than that of bromide. This can result from the effect of size exclusion. Due to their size, bacteria preferentially follow the flow paths consisting of bigger pores with larger flow velocities, resulting in relatively earlier breakthrough of bacteria. The relative peak concentration of bacteria, however, is much lower than that of bromide and exhibits a much longer tail. Bacterial concentrations level off after about 3 pore volumes (about 400 minutes) but last up to about 38 pore volumes (not shown in the figure). Mass recovery of the first 3 pore volumes was only 48.64%. We sampled for about 90 hours (38 pore volumes) and the last sample taken still had a concentration of about 10^5. Bacteria were retarded in the sand by sorption or filtration and were flushed out slowly for long periods of time.

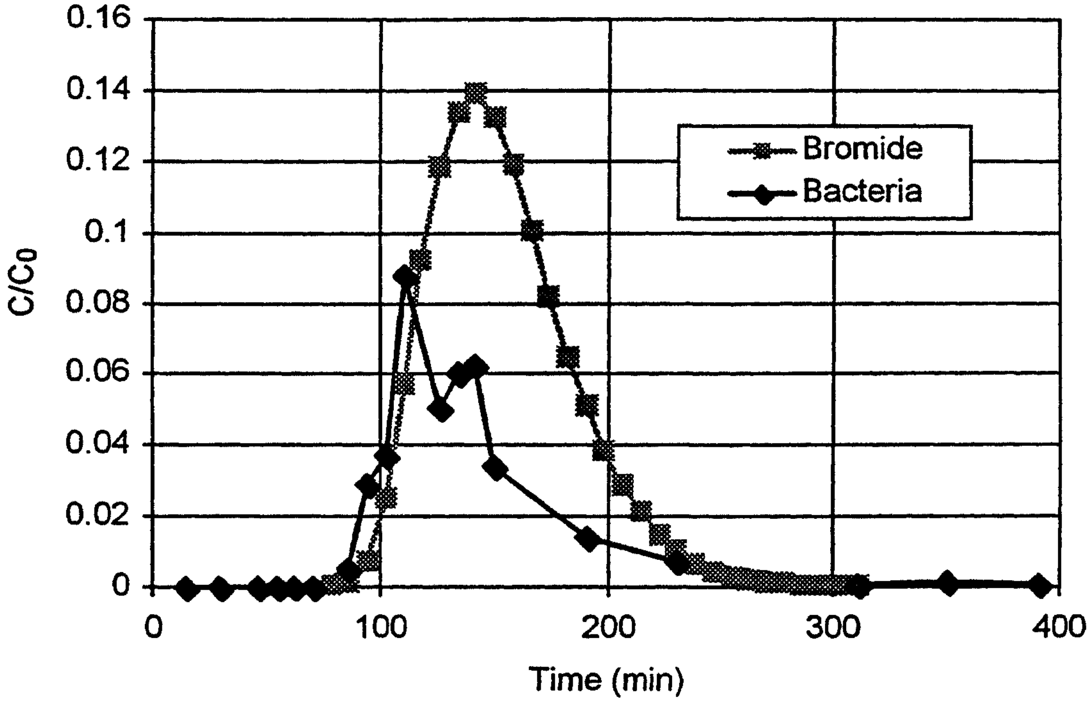


Figure 6. Bacterial breakthrough curve in comparison with bromide breakthrough curve.

Table 4. Comparison of bacterial and bromide breakthrough through quartz sand.

	C_{max}/C_0	C_{max} arrival Time (min)	Mass recovery (%)
Bromide	0.1395	142	101.10
Bacteria	0.0372	102	48.64*

*Mass recovery of the first 3 pore volumes.

Based on the results of both bromide and bacterial flow-through experiments, it is clear that the new column setup is working as expected. Now that the new experiment setup has been verified, we will begin to collect natural sediments and perform flow-through experiments on natural cores.

Investigation of Autochthonous Microbial Community

Groundwater aquifer sediment has been and continues to be analyzed so that the microbial biomass and microbial community structure can be characterized. Sediments are also being analyzed for sediment grain size. We hypothesize that there is variability in microbial biomass and the microbial community structure at differing depths that is related to grain size. In fact, it appears that there is a relationship between biomass and the location of interfaces of two distinct sediment types.

To test these hypotheses, three sediment cores were extracted from a field site near Four Mile Creek and the Water Treatment Facility in Oxford, OH. The 5/13/98 and 8/20/98 bore holes were drilled to the base of the aquifer using hollow-stem augers. The 1/22/99 bore hole was drilled using a hydraulic drill rig supplied and operated by Geoprobe Systems. The 5/13/98 and 8/20/98 cores were retrieved using a sterile split-spoon sampler, and the 1/22/98 core was recovered in a sterile plastic liner. Samples were taken from the sediment cores at 0.6m intervals, and at sediment interfaces. Sediment samples were also taken immediately above and below the biological sampling sites for grain-size analysis. For biological sampling, the outside of the core was removed and samples were taken using a sterile spoon. These were placed in sterile test tubes and kept on ice in the field for no more than 8 hours, then brought to the laboratory for biological analysis. The microbial lipids were then extracted using a modified Bligh-Dyer lipid extraction (3, 10, 26). Once harvested, a portion of the lipid was analyzed in a colorimetric assay for the amount of phospholipid phosphate (PLP) present. This amount was quantified spectophotometrically, and converted to microbial biomass. The remaining lipid was partitioned on a silicic acid column. The phospholipid fraction was collected, and the glycolipid and neutral lipid fractions were discarded. The purified phospholipids underwent a mild alkaline methanolysis, and the resultant fatty acid methyl esters, (FAMEs) were purified using a C18 column. These FAMEs were then analyzed with gas chromatography. The presence, absence and abundance of certain fatty acids were analyzed and used to determine the types of microorganisms present in the sample (7, 9, 25).

Two of the three sediment cores have already been processed for PLP. The data obtained from the PLP analysis have been used to determine microbial biomass profiles (Figures 7 and 8). Both sediment cores displayed large variations in microbial biomass with depth. At the different depths sampled, the 5/13/98 core's biomass varied between 0.13 and 0.56 nmol PLP/g DW. The 8/20/98 core's biomass was highest in samples taken above 2.8 m below the surface. Below 2.8 m, there was variation at the different depths sampled similar to the 5/13/98 core.

PLFA data were used to determine microbial community structure. Fatty acids present were predominately 14-19 carbons in length and included saturated, straight-chained fatty acids 14-18 carbons in length, terminally-branched fatty acids, branched, monoenoic fatty acids and straight-chained, w 5,7,and 9 monoenoic fatty acids. Unusually abundant fatty acids were 16:1ω5, 10me16:0, cy17:0 and several branched 19:0 fatty acids. PLFAs including 10me16:0 and the branched, odd-chain fatty acids indicated the presence of anaerobic bacteria including sulfate-reducing bacteria. The polyenoic fatty acids 20:4w6 and 20:5w3 occurred at low abundances. This indicated that the microbial community contained heterotrophic microeukaryotes and that these organisms were a minor component of the community.

Microbial biomass and community structure for the third core will be analyzed using PLP and PLFA analysis. Grain size analyses of the second and third cores are being conducted to determine the sediment characteristics at the same depths where the biological samples were taken. By combing these data with the abiotic conditions of the aquifer, a description and location of the autochthonous microorganisms will be correlated with various groundwater sediment types. This novel data set will provide a basis for future work involving the prevention of groundwater contamination and the remediation of contaminated aquifers.

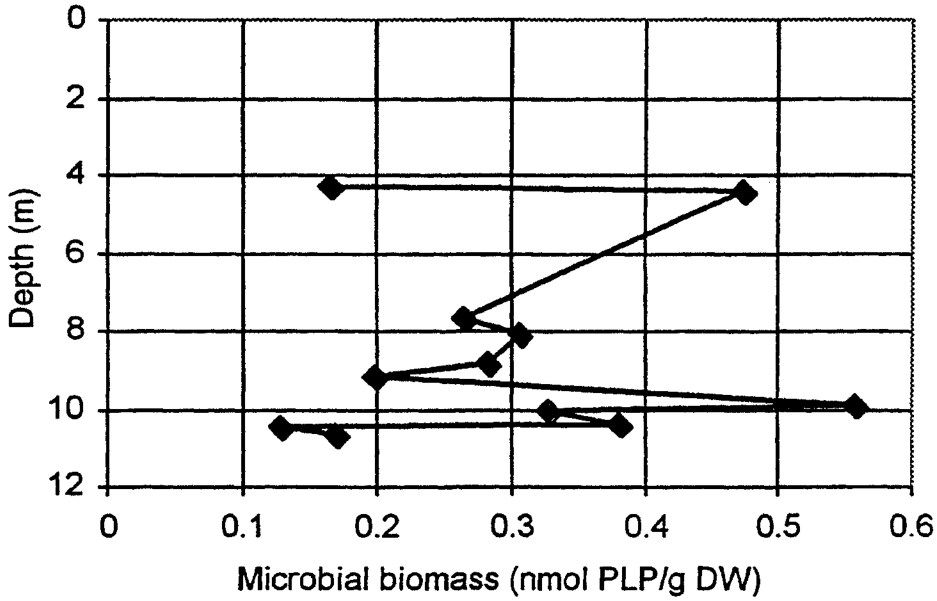


Figure 7. The microbial biomass profile for a groundwater sediment core taken on 5/13/98.

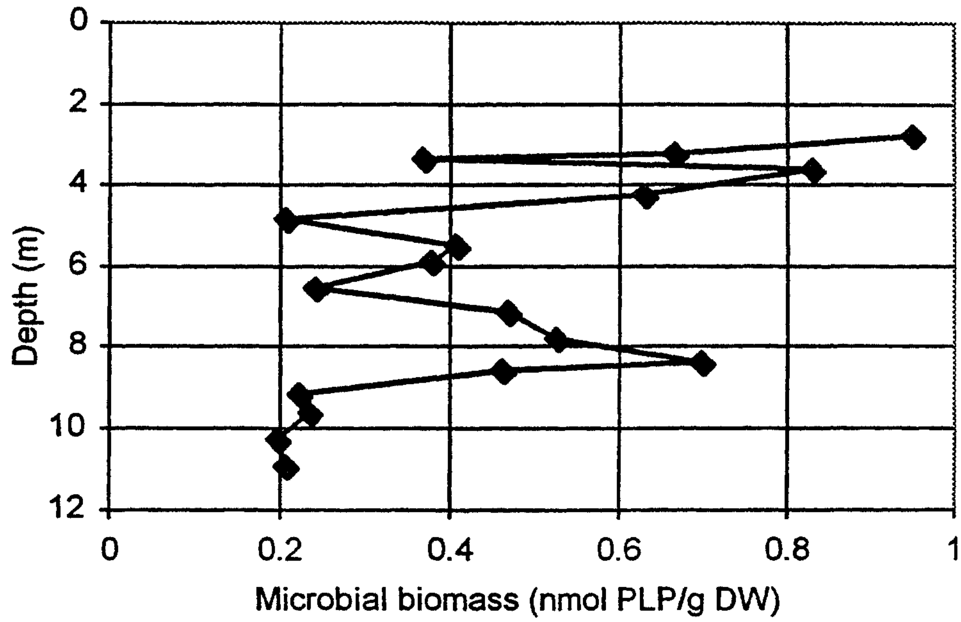


Figure 8. The microbial biomass profile for a groundwater sediment core taken on 8/20/98.

Hypothesis 3: Progress and results associated with establishing the field site

Site Description

Four Mile Creek Valley area bedrock lithology is characterized by interbedded limestone and shale of Ordovician age. During the early Pleistocene, a river carved a valley into the bedrock. The valley was carved to far greater depths than present elevation. During the Pleistocene, glaciers advanced and retreated, filling the valley with alternating layers of sand and gravel glacial outwash and dense glacial till. The result is a heterogeneous sediment sequence of coarse and fine layers. The shallowest layers are highly permeable sands-and-gravels with some silt and cobbles. The aquifer of interest for this study is the shallow, unconfined aquifer lying above a thick, impermeable layer of glacial till.

The specific field site of interest within the Four Mile Creek valley is located adjacent to Four Mile Creek, less than one mile east of Oxford, Ohio, adjacent to State Road 73 (Figure 9). A municipal pumping well was installed at this site in 1961. This municipal well is a Ranney collector (Figures 9 and 10), comprising a central vertical caisson equipped with a pump. From the base of this caisson, radial arms extend horizontally into the aquifer. When pumping, drawdown in the central caisson induces flow of water from the aquifer into the radial arms and into the caisson where it is pumped to the water treatment plant.

The radial arms vary in length and depth (Figure 10). The depth of the upper

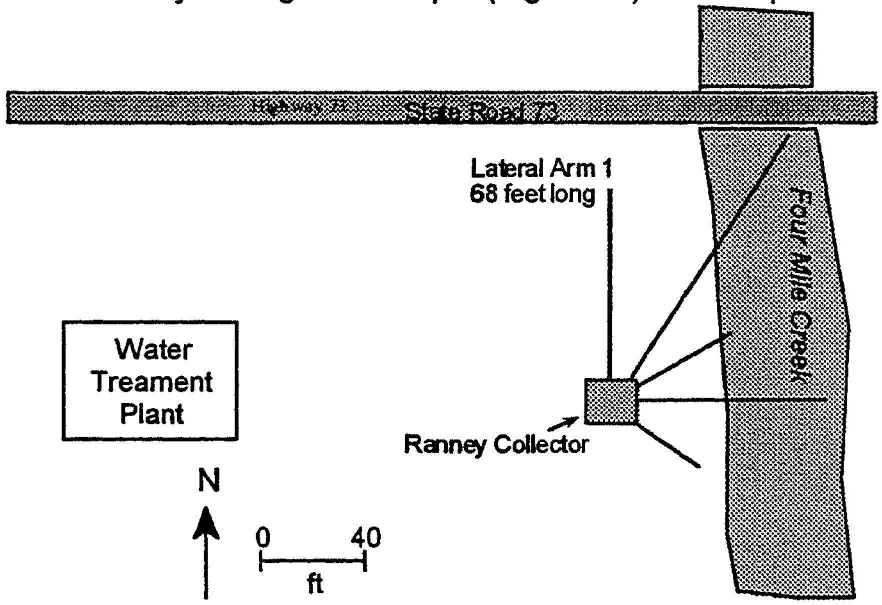


Figure 9. Plan view of Ranney collector and field site.

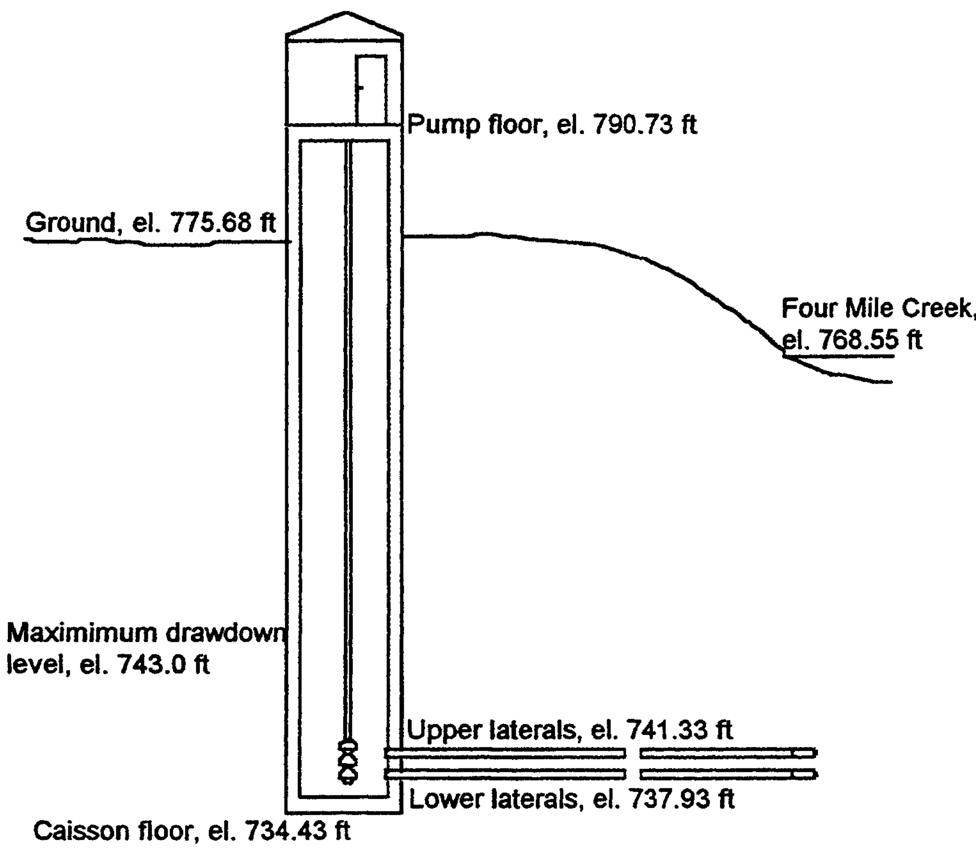


Figure 10. Profile view of Ranney construction.

laterals is less than 50 feet below the bed of Four Mile Creek. According to US EPA standards, this municipal well is considered to be under the direct influence of surface water in Four Mile Creek.

In 1996 the Ranney production well was taken offline due to the presence of coliform bacteria in water samples. The City of Oxford has allowed the use of this well and surrounding area as a research site to examine the fate and transport of bacteria from Four Mile Creek to the municipal well.

Design and Development of Field Site

At the beginning of this project, Laterals 1 and 2 were open; the rest were closed. Because Lateral 1 is parallel to the creek, we wanted only that lateral open to induce flow perpendicularly from the creek to the lateral. Therefore, in December 1998 we contracted Reynolds, Inc. to dive into the caisson and close off Lateral 2.

Placement of monitoring wells was based on the stream-pumping well configuration and expected flow paths. Ten monitoring wells have been installed using a hollow-stem auger drilling rig (Figure 11). The monitoring wells were installed in 5 nested pairs: TS1A&B, TS2A&B, TS3A&B, TS4A&B, and TS5A&B, where the "A" wells are approximately 8-10 feet shallower than the "B" wells. Multilevel sampling wells – TS6, TS7 and TS8 – were also installed (Figure 11). The monitoring wells consist of 1.25 inch diameter PVC casing with a 1-ft long screened interval of 20 slot screen at the bottom. The multilevel sampling wells are StrataSamplers® manufactured by Timco, Inc. They consist of 2-inch diameter, 1-ft long screened interval stainless steel with a sediment sump. Three-foot long, 2 inch diameter PVC casing separates the sampling ports.

The heterogeneity of the aquifer sediments were characterized by analyzing sample cores. Some samples were acquired by drilling with a hollow-stem auger rig, capable of drilling to a depth of 45 ft below ground surface. The sample cores were taken with a 2-inch diameter steel split-spoon sampler. Other samples were acquired by a direct hydraulic push system designed by Geoprobe Systems and a 1.5 inch diameter split spoon sampler at boreholes GP1 and GP2. Using the Geoprobe system, downhole electrical conductivity data was also collected at boreholes GP1, GP2, GP3, GP4, GP5 (not shown) and GP6 (not shown). The electrical conductivity profile for GP1 was used for calibration against an actual sediment log. Using GP1 as a benchmark, lithology for the other GP boreholes was inferred from the conductivity profiles.

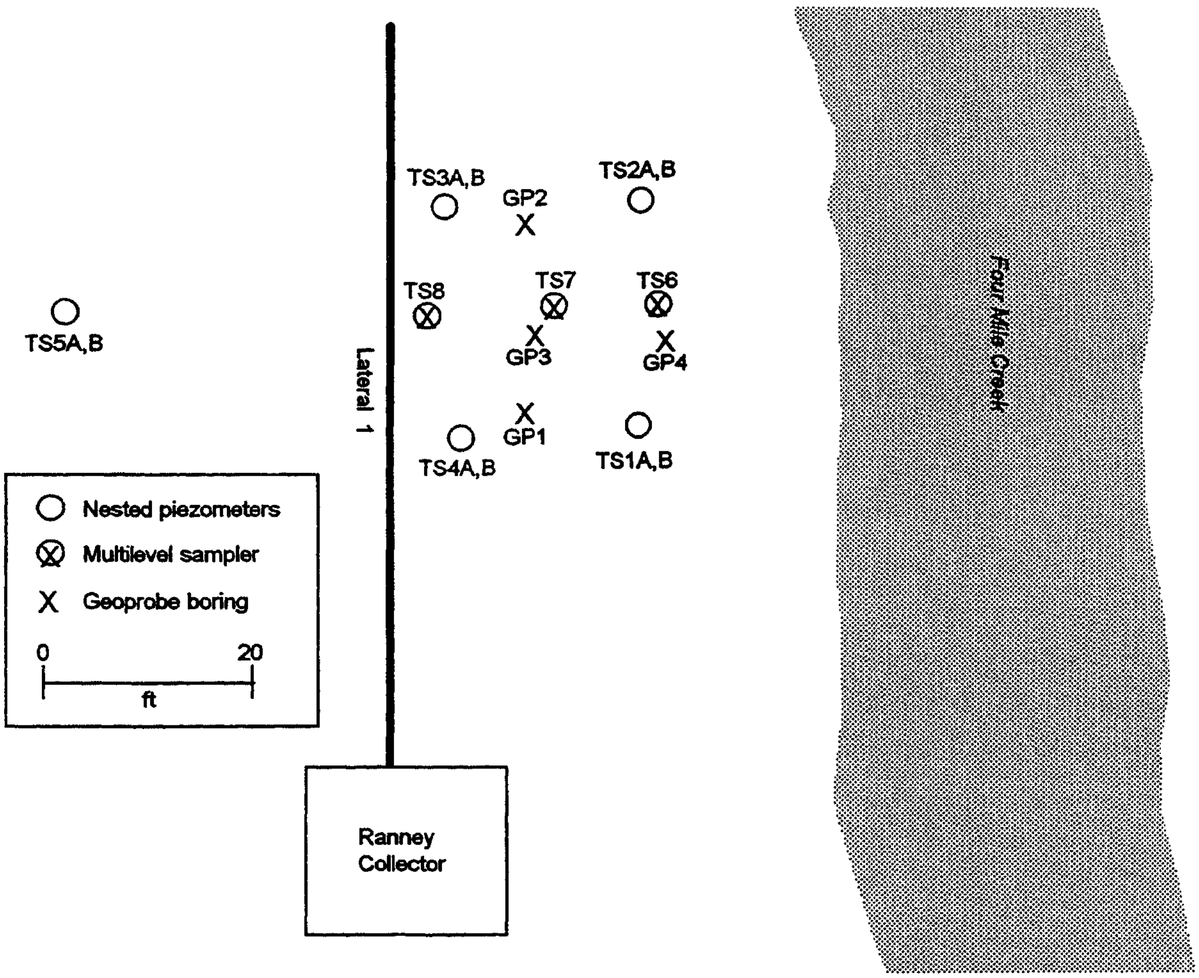


Figure 11. Locations of monitoring wells and Geoprobe borings.

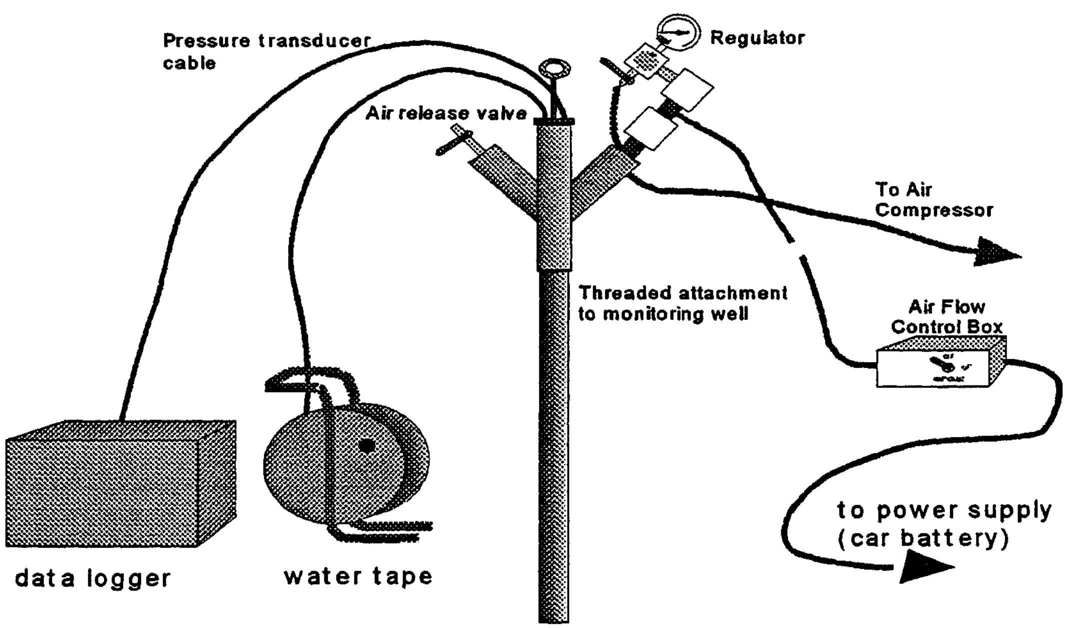
Piezometer Slug Tests

Slug tests provided estimations of hydraulic conductivity on the scale of approximately 3-15 ft – larger than that of the column permeameter experiments, but smaller than most aquifer pumping tests. Multiple slug tests were performed at each piezometer to demonstrate reproducibility of response curves at the same and different displacements (Butler, 1998).

Due to the high hydraulic conductivity of the formation, many of the slug tests exhibited oscillatory behavior caused by the inertial energy and momentum of the water column. (Springer and Gelhar, 1991). These tests were analyzed using a method by Springer and Gelhar (1991). The method uses curve matching to Kipp type curves (Kipp, 1985). Tests not exhibiting the oscillatory behavior were analyzed with the method by Bouwer and Rice (1976).

The delivery of the "slug" or change in water level in a slug test must be done instantaneously. Traditional methods where a volume of water is displaced or removed create complications of splashing and spilling thus resulting in a non-instantaneous slug. We therefore developed a pneumatic apparatus in which air pressure is used to lower the water level. A large diameter, quick release valve allows instantaneous release of the pressure. A pressure transducer located at the screened interval of the well measures the recovery. The design for the slug test can be seen in Figure 12. It consists of an airtight cap that fits over the top of a 1-inch well top, a port for the pressure transducer cord and water level sensor, a port for the air intake regulator, and a port for an air evacuation valve. The intake air valve and regulator are connected to an air compressor. To ensure that the water level is not pushed below the pressure transducer, the water level sensor is lowered to the depth of the maximum induced head change, with the pressure transducer at a greater depth. The water level is lowered slowly until the water sensor beeps. At this point the water level is held constant by the regulator. The data logger is started and the pressure is then instantaneously released.

Figure 12. Diagram of air-slug apparatus.



Values of hydraulic conductivity obtained from these analyses ranged from 70 to 607 ft/day (0.050 to 0.214 cm/sec) with an arithmetic mean of 329 ft/day and a geometric mean of 275 ft/day (Table 5). No wells were screened in the shallow fine layer; the range of values reflects only hydraulic conductivity within the outwash deposits.

Oscillatory responses were found in TS4A, TS4B, TS5A, and TS5B. The values of hydraulic conductivity found for these wells were higher than in most of the other wells. Sediment samples taken at the screened intervals of the highest conductivity boreholes (TS4B and TS5B) showing oscillatory responses were characterized in the field as being a fairly well sorted coarse sand and gravel with little to no fine sand or silt. Grain analysis showed that a sample taken at the screened interval of TS5B was 2% gravel, 90% sand, and 8% silt/clay. Field descriptions of sediment samples obtained from the screened intervals of the other boreholes were characterized by more poorly sorted sand and gravel with a larger percentage of fine sand or silt.

Aquifer Pumping Tests

A larger scale measurement was obtained by conducting an aquifer pumping test. Due to the unusual configuration of the lateral pumping arms and the creek, the hydraulic conductivity cannot easily be solved for using classical analytical methods. Instead, we have solved for hydraulic conductivity numerically by designing and calibrating a flow model to steady-state non-pumping and pumping conditions.

Table 5. Summary of hydraulic conductivity values from slug tests.

Piezometer	K (ft/day)	K (cm/sec)
TS1A	141	0.050
TS1B	394	0.139
TS2A	121	0.043
TS2B	70	0.025
TS3A	359	0.127
TS3B	341	0.120
TS4A	342	0.120
TS4B	398	0.140
TS5A	375	0.132
TS5B	557	0.197

A pumping test was conducted February 4, 1999 with only Lateral 1 open to the aquifer. This test was run for 50 hours at a pumping rate of 40.65 ft^3/min. During this time, the groundwater system appears to have reached or nearly reached steady state. Based on calibration of the groundwater-flow model the pumping-test data yield a hydraulic conductivity for the outwash sediments of 440 ft/d. This value is somewhat higher than the slug-test geometric mean of 275 ft/d. The groundwater-flow modeling is described in detail below

Tracer Tests

On approximately the same scale as the pumping test, a conservative tracer test is being designed to attain another value of hydraulic conductivity, likely to be most representative of movement of groundwater from Four Mile Creek to the Ranney collector. The design of the tracer test will consist of injection wells closely spaced in the creek near the edge at a depth of 3-5 feet below the creek bed. The multilevel sampling wells have already been installed along predicted flow paths from the creek to

Lateral 1. Sampling ports were installed at evenly spaced depths positioned to intersect the tracer's flow path. Tracer tests are scheduled to begin in August 1999.

Groundwater Flow Modeling

In this study, a flow model was developed to attain numerical solutions for aquifer pumping tests and predict contaminant flow paths from the creek to the Ranney collector.

1. Conceptual Model. The aquifer being modeled was considered an unconfined system. The upper boundary of the aquifer is therefore the water table. The bottom of the aquifer is the impermeable glacial till layer. The western and eastern boundaries of the modeled area are the Four Mile Creek valley walls. The north and south boundaries were set far from the zone of influence of the pumping. The uppermost stratum is composed of brown, organic-rich, soil which grades into brown silt, sand and gravel. This layer is underlain by a gray, fine-grained layer characterized by very high clay and silt content. This layer was assumed to be horizontally continuous, consistent with drilling core logs. Beneath the fine layer is a sand-and-gravel layer. This layer has lenses with higher percentages of cobbles, gravel and sand. Four Mile Creek runs generally north to south across the area. Recharge was assumed to occur at a constant rate over the entire land surface.

2. Model Code and Grid Discretization. MODFLOWwin32 was the program used to numerically simulate the groundwater flow. Grid cells are as large as 30 ft by 30 ft but telescope down to as small as 5 ft by 5 ft in the area of the Ranney collector and monitoring wells. Such a fine grid was needed to differentiate between different monitoring wells in the area of interest and to properly simulate pumping in Lateral 1. The model consists of seven layers. Layer thicknesses were determined by examination of drilling core logs. The lower boundary is the impermeable till. Layers 3-7 represent the glacial outwash and are modeled with a homogenous value of hydraulic conductivity. Layers 3-7 are either 4 or 5 feet thick for the purpose of representing varying depths of the monitoring wells' screened intervals and the depth of the pumping well lateral arm. Layer 2 represents the fine grain facies of silt/clay and is continuous and assumed homogeneous across the study area. Layer 2 is modeled as 5-ft thick, which represents an average thickness of this layer. Layer 1 represents the sediments above the silt/clay layer. From core sample data, this layer typically grades from silty top soil to sand and gravel. It is modeled with a homogeneous value of hydraulic conductivity.

3. Stream-Aquifer Interaction. Four Mile Creek was modeled using measured stream width, depth, and streambed and stream stage elevation data. MODFLOW's river package was used to simulate the interactions between Four Mile Creek and the aquifer. The river was modeled with a gradient of 0.002, width of 65 ft, depth of 2 ft, length of 164 ft, stream bed thickness of 1 ft, stream bed conductivity of 2.62 ft/day, and stream conductance of 2.49×10^4 ft^2/day.

4. Initial Parameter Values. The value for recharge rate was set to approximately 1/3 the average annual precipitation rate (0.003 ft/day). Initial values for hydraulic conductivity were estimated based on slug test measurements and sediment size and distribution.
Vertical hydraulic conductivity values were based on the assumption of the anisotropy (K_v/K_h) ratio of 0.1. Other parameter values were based on the literature. All of the initial values are summarized in Table 6.

5. Calibration. The goal in calibration of the model was to match the field-measured target points in the modeled area. The model was calibrated in two phases. First it was calibrated to a set of targets on January 31, 1999 when there was no pumping. During this calibration, the model was insensitive to changes in parameter values. The model was then calibrated to a set of targets achieved at the end of the February 4, 1999 aquifer pumping test. This model was much more sensitive to changes in values of hydraulic conductivity. Table 6 shows the calibrated model parameter values.

Table 6. Summary of calibrated model parameters.

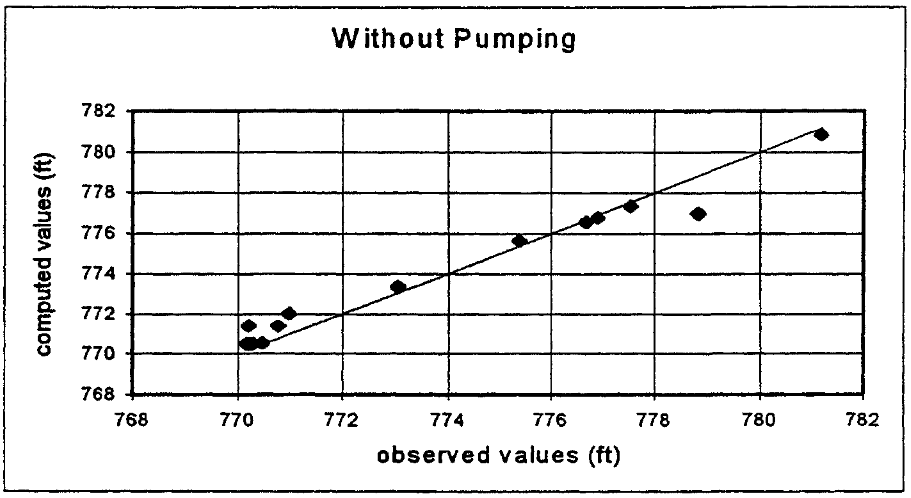
Parameter	Initial value	Calibrated value
Layer 1 K_h (soil and outwash)	190 ft/day	231 ft/day
Layer 1 K_v (soil and outwash)	19.0 ft/day	21 ft/day
Layer 2 K_h (silt and clay)	1 ft/day	1 ft/day
Layer 2 K_v (silt and clay)	0.1 ft/day	0.225 ft/day
Layer 3-7 K_h (outwash)	279 ft/day	440 ft/day
Layer 3-7 K_v (outwash)	27.9 ft/day	58.08 ft/day
Recharge rate	0.003 ft/day	0.003 ft/day
Well discharge rate	58608 ft^3/day	58608 ft^3/day
Stream bed conductance	2.49×10^4 ft^2/day	2.49×10^4 ft^2/day
Effective porosity	0.3	0.3

Summary statistics to evaluate the accuracy of the model in predicting the measured head values are shown in Table 7. The residual refers to the difference between measured and simulated heads. Figure 13 shows the model-predicted head values plotted against the observed values for nonpumping and pumping scenarios. The points plot close to the one-to-one trendline. The well with the greatest residual is FC5. The reason for its large residual is unknown, but the well is far outside the area of pumping.

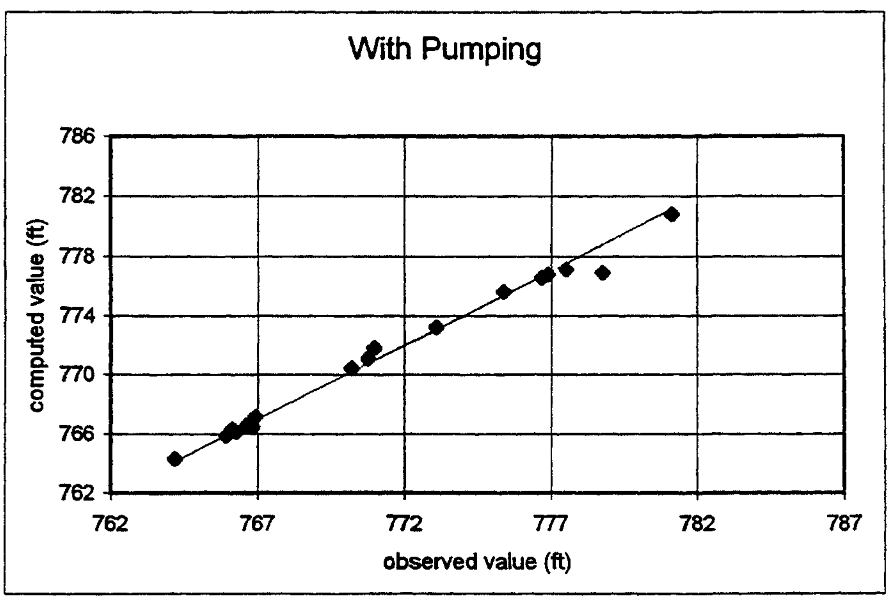
Table 7. Summary of statistics for pumping and nonpumping scenarios.

Statistic	Nonpumping	Pumping
Residual Mean (ft)	-0.14	0.07
Residual Sum of Squares (ft^2)	7.04	5.10
Absolute Residual Mean (ft)	0.45	0.35
Minimum Residual (ft)	-1.19	-0.83
Maximum Residual (ft)	1.85	1.88
Head Range (ft)	11.01	17.02

a. Figure 13. Model-predicted (computed) versus observed heads during a) pumping and b) nonpumping conditions.



b.



6. Sensitivity Analysis. A sensitivity analysis was performed to assess which parameters are most influential in model calibration. Both the pumping and nonpumping scenarios are sensitive to changes in K_h of the silt/clay layer and the outwash layer. The model with pumping is far more sensitive than the non-pumping model since the drawdown created by the pumping is dependent on hydraulic conductivity. The calibrated values of K_h are optimal (in terms of minimizing the residual sum of squares) for all three facies in the pumping model. With the non-pumping model, the calibrated values are optimal for the uppermost top soil layer and the silt/clay layer. For the sand-and-gravel layer under nonpumping conditions, a lower value of K_h would be optimal, but only slightly improves the calibration. The high degree of sensitivity allows a high degree of confidence in the calibrated K_h values of those two facies.

The model was insensitive to increases in K_v in both scenarios. The non-pumping scenario is highly sensitive to a decrease in K_v of the silt/clay layer. The model with pumping is sensitive to decreases in K_v of the sand-and-gravel outwash layer as well. The calibrated value is nearly optimal in both scenarios.

The model with no pumping is sensitive only to an increase in recharge rate. The pumping model is only sensitive to the pumping discharge rate. The calibrated recharge and pumping rate values are also optimal.

7. Use of the Flow Model as a Predictive Tool for the Tracer Test

The flow model can be used to investigate solute transport within the flow domain. Using MODPATH allows particles to be placed anywhere within the flow domain and their paths to be predicted. Since the tracer test will be performed only under pumping conditions, that will be the focus of the MODPATH simulations. Prediction of the transport of particles placed below the streambed along the western edge of Four Mile Creek shows a nearly perpendicular flowpath from the stream to Lateral 1. Multilevel sampling wells were installed along a transect that follows this flowpath.

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C. PUBLICATIONS

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Sun, K., A.J. Rossman, J. Levy, R.H. Findlay and H.L. Schran (1998) Bacterial transport through intact sediment cores: variability of transport parameters and controlling aquifer characteristics. Abstract 51051, 1998 Fall meeting of the Geological Society of America.

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Findlay, RH, H.L. Schran, A.J. Rossman, J. Levy (1998) Microbial community structure of a shallow groundwater sediment and coliform bacterial transport. Abstract for the Joint Meeting of the Ohio & West Virginia Branches of the American Society for Microbiology, April 24-25, 1998, Ohio State University, Columbus, OH.

SYNOPSIS

PROJECT NUMBER: C-07 **Start:** 9/1/98
End: 8/31/00

TITLE: Sonochemical Remediation of PCB Contaminated Sediments

INVESTIGATORS:

Lead P.I.: Linda K. Weavers, The Ohio State University
Co-Investigator: Yu-Ping Chin, The Ohio State University

CONGRESSIONAL DISTRICT: Fifteenth

FOCUS CATEGORIES: TRT, SED, TS

DESCRIPTORS: Contaminated Sediment, Remediation, Surface Water Quality, Oxidation, Toxic Substances

PROBLEM AND RESEARCH OBJECTIVES:

In December 1997, EPA released the report, "The Incidence and Severity of Sediment Contamination in Surface Waters of the United States" documenting the severity of sediment contamination. Of the 96 Areas of Probable Concern, 39 are located within nine states in the North Central Region, many contaminated with polychlorinated biphenyls (PCBs) (US EPA, 1997b) . For example, the Ottawa River in Ohio has a fish consumption advisory in effect due to PCB levels more than 30 times the USFDA health standard for fish filets. Moreover, the EPA estimates that in the United States approximately 10% of the sediment underlying surface waters is sufficiently contaminated to pose risks to fish, humans, and wildlife (Bolattino and Tuchman, 1993) . It is difficult to treat sediments or soils because the sorbed hydrophobic contaminants are less accessible. Currently, capping the sediments in place or extraction and removal to a hazardous waste landfill is the most common method of treatment. However, the contaminants are not destroyed and pose a potential future risk. Moreover, episodic events such as storms and ships may compromise the capping material (by re-suspension) which could potentially mobilize the contaminants.

One of the EPA's four goals for managing contaminated sediment is to better understand the fundamental processes involving contaminated sediment and to develop solutions (US EPA, 1998) . Ultrasonic irradiation of contaminated sediments may provide an on-site treatment technology that removes the contaminant from the sediment and subsequently destroys the contaminant through sonochemical oxidation. Research into the fundamental factors affecting sonochemical remediation of contaminated sediments will increase the understanding of this potential treatment process as well as lend insight into the factors affecting desorption of contaminants from sediments.

The development of this treatment technology will provide an alternate solution to existing sediment remediation technologies. Existing treatment technologies such as capping have the limitation that the pollutants are not destroyed and pose a future risk. Incineration is also used, but is prohibitively expensive and labor intensive. Conversely, sonication of sediments can be performed on a ship, does not require dewatering, and since sonication destroys the contaminants, the sediments can be replaced after treatment. The proposed process is potentially more energy efficient and environmentally benign than conventional sediment remediation technologies.

The purpose of this project is to investigate the application of ultrasound to sediment polluted with PCBs. PCBs are an EPA priority pollutant and persist in the environment due to their unreactive nature. They are extremely hydrophobic and tend to partition from the aqueous phase to the gas or solid phase. Ultrasound applied to polluted sediment is a two-step process. First, the physical effects of acoustic cavitation have the potential to clean the sediment surface by the jets of imploding cavitation bubbles impinging on the particles and shear forces from microstreaming near the particle surface. Then, the PCBs will preferentially partition to the cavitation bubble (due to its high octanol/water partitioning coefficient (log $K_{OW} > 5$) and high Henry's Law constant ($H \sim 50$ Pa m^3 mol^{-1})) where they will be destroyed by pyrolysis or oxidation with OH• radical. In this proposed remediation process, the sediment does not need to be dewatered and dried for remediation. Also, this process is transportable and has the potential to be used on a ship as dredging occurs.

Specifically, the *goals of this research are:*

1) to demonstrate the ability of sonication to remove PCB from synthetic and natural sediments;

2) to show that sonochemical techniques destroy the PCB once it enters the soluble phase;

3) to characterize the role of sediment matrix parameters in sonochemical remediation; and

4) to identify key design variables in the sonochemical remediation of contaminated sediments.

METHODOLOGY:

PCB Removal from Model Systems

Due to the complexity of natural systems it is often beneficial to investigate well-characterized systems prior to the use of more complex matrices such as sediments. We have begun to study the removal of a model PCB, 4-chlorobiphenyl (4-CB), from solid particles. Comparing the sonochemical desorption from minerals such as illite, hematite, and manganaese dioxide, and three different size silica gels, we will be able to determine relative effects of surface area, particle diameter, and internal pore size. The solids will be characterized for particle diameter, surface area, pore diameter, and organic content. In addition, in a set of experiments, various concentrations of humic substances (e.g., IHSS material) will be sorbed to the particles prior to 4-CB sorption in order to determine the effect of organic matter on ultrasonic desorption and destruction of 4-CB. 4-Chlorobiphenyl will be sorbed onto the particles over a period of at least 3 days or until apparent short term saturation is reached.

For sonochemical experiments a 20 kHz Probe sonicator or a 16 and 20 kHz Near-Field Acoustical Processor (NAP) will be used. The reactors are temperature controlled with a water jacketed reactor and circulating constant temperature bath. Reactors are specially designed and the reacting solution will be continuously stirred to keep the solids in suspension. The sonochemical energy entering the reactor will be measured by calorimetry. Dosimetry will also be performed to determine the effect of solids on radical formation.

In order to properly characterize the sonicating system, many controls will be performed. Initially, PCB destruction kinetics will be performed in the absence of solids under controlled conditions. Additionally, vigorous stirring at a constant rate with 4-CB laden solids will enhance desorption processes (through shearing effects) in the absence of sonication. The effect of solids on the absorption of ultrasonic waves into solution and bubble dynamics will be measured by calorimetry and iodide oxidation in our blank experiments. Due to safety concerns, experiments with 4-CB will be conducted only in the small probe sonicator. The effectiveness of the NAP in sonochemical desorption will performed by correlating particle size changes and OH radical generation in the two reactors.

We will study the effect of 4-CB destruction in the presence of well-characterized solids as discussed previously. 4-CB will be monitored in the solid and aqueous phases as a function of time for each experiment. In both of these systems matrix parameters such as pH, temperature, and ionic strength will be controlled. Once destruction and desorption kinetics have been established, parameters such as physical characteristics of the particle, particle concentration, and humic acid concentration will be varied to determine optimal conditions and effects.

Aqueous phase and solid phase samples will be extracted hexane. Solids will be separated from liquid phases by centrifugation. A gas chromatograph coupled with electron capture detector (GC-ECD) will be used to follow 4-CB concentrations for the duration of the experiment. Finally, 4-CB derivatives formed from sonolysis will be followed using gas chromatography with an ion selective mass spectrometer (GC-MS).

The violent nature of cavitation may shear particles, remove organic matter coating, disperse aggregates and dissolve aggregates. To observe this effect, the particle size, solution composition, and surface will be monitored. Scanning electron microscope (SEM) techniques will be used to investigate changes in the surface of the solids brought about by ultrasonic irradiation. In addition, a particle size analyzer will monitor the relative size distribution of the solids. Finally, ion-coupled plasma-mass spectrometry (ICP-MS) will be used to determine if dissolution of particles is occurring.

PCB Removal from Natural Contaminated Systems

After the process is characterized in the well-controlled system, contaminant removal and destruction from actual sediments will be explored. Sediment will be collected from three sites: the Ottawa River located in Northern Ohio; the shipping channel of the Cuyahoga River in Northeastern Ohio; and where Fields Brook flows into the Ashtabula River in Northeastern Ohio. All of these sites are contaminated with various amounts of PCBs as well as other organic and inorganic species (Bolattino and Tuchman, 1993) . Near-shore clean and contaminated samples will be obtained with an Eckman sampler. Standard on-site analysis will be conducted for parameters such as dissolved oxygen, pH, and temperature. Samples will be transported to the laboratory in amber glass jars with Teflon screw caps at 4 °C. The sediment will be characterized for particle size distribution, organic matter content, and reactive inorganic species such as iron. Organic contaminants will be extracted as described in McGroddy et al. (1996) and quantified by GC-MS.

After investigating the 4-CB model system, spiking the model contaminant on a clean sediment similar to the contaminated system may help compare the model system to the natural system as well as give us insight into controlling factors in the natural system. For example, the model system will use a monodisperse particle size whereas the river sediments will have a size distribution and range of pore diameters. Clean sediment samples will be spiked with 4-CB and removal and destruction will be monitored. Contaminated sediments will then be subjected to sonication. PCBs and byproducts will be followed in aqueous solution and in the sediment by GC-MS. NOM released into solution will be monitored by total organic carbon analysis (TOC). In addition, with a particle size analyzer, the particle size distribution will be followed throughout the duration of each experiment.

PRINCIPAL FINDINGS AND SIGNIFICANCE:

In September 1998, Yifang Lu, the graduate student on the project arrived at The Ohio State University. She began research immediately while taking graduate courses.

In the fall equipment required for this project including a probe sonicator, NAP, circulating water-bath, Teflon double diaphragm pump, and GC-ECD were installed in the laboratory. In addition, specialized reactors to run sonochemical experiments were designed and built in the OSU Glass Shop.

Preliminary experiments and controls were conducted in the first 6 months of this project. An analytical technique to remove 4-CB from particles using hexane extractions and detection on the GC-ECD was developed. This technique is under refinement to obtain accurate mass balance of 4-CB. A method was developed using the Mastersizer particle sizer to investigate changing particle sizes during sonication. Proper lens cleaning and sampling and stirring protocols were developed to obtain accurate and reproducible results. Various techniques were employed to sorb 4-CB to silica and hematite. These experiments resulted in essentially no sorption of 4-CB to bare particles under our specified conditions. Efforts continue in this area to determine appropriate pH buffers and solution conditions to obtain reproducible results. In addition, the selection of an appropriate series of particles to best understand anticipated effects continues. Furthermore, in these initial experiments, particle dispersion was problematic. In an attempt to keep particles dispersed throughout the duration of a sonication experiment, a new probe reactor will be designed. Finally, the destruction of a 5 uM 4-CB solution was performed in the absence of particles in the probe sonicator.

In a complementary effort Nicolas Riyanto, a chemical engineering undergraduate student was recruited to conduct an honors thesis project during year 2 of this project. He will focus on determining the OH radical concentrations in the presence of different particles (both chemically and physically different) to determine particle effects on OH radical generation.

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STUDENT SUPPORT:

Yifang Lu, master of science student in Department of Civil and Environmental Engineering and Geodetic Science

Nicolas Riyanto, undergraduate student in Department of Chemical Engineering (to begin autumn 1999)

SYNOPSIS

Project Number: C-08

Start Date: 09/98
End Date: 08/00

Title: Enhanced Removal of DEP Precursors During Precipitative Softening Through Co-Adsorption Processes

Investigators: Harold W. Walker, Department of Civil and Environmental Engineering and Geodetic Science, The Ohio State University

Congressional District: 15th

Focus Category: TRT, SW, WQL

Descriptors: Disinfection By-Products, Waste Treatment, Softening, Natural Organic Matter, Precipitation

Problem and Research Objectives : The chlorination of drinking water can result in the formation of disinfection by-products (DBPs) such as trihalomethanes and haloacetic acids [i]. DBPs are probable carcinogens, and short-term exposure can lead to dizziness, headaches, as well as problems associated with the central nervous system. Recent studies have also linked DBPs to increased incidence of miscarriage [ii], rectal and bladder cancer [iii, iv], and neural tube birth defects [v]. As a result of the health effects associated with DBPs, as well as microbial pathogens, nearly 40% of water treatment plants in the United States will have to upgrade their systems by 2001 at an estimated cost of $10 billion [vi]. It is estimated that 80% of water treatment facilities will have to make changes to meet regulatory requirements by the year 2005.

In the state of Ohio, 125 water treatment plants utilize lime softening for the removal of hardness and turbidity [vii]. To be in compliance with upcoming United State Environmental Protection Agency (USEPA) regulations regarding DBPs, these and other lime softening plants around the country will be required to remove 20-30% of the natural organic matter present in their source water [viii]. Improvements in the removal of organic matter will most likely be accomplished through alteration of the softening process (so-called "enhanced precipitative softening"), or through the addition of unit operations such as activated carbon. Enhanced softening involves raising the amount of lime added during treatment (roughly 5 to 10 times) and subsequently results in greater chemical costs and the increased production of sludge.

Although enhanced softening results in greater precipitation of $CaCO_3$, previous research indicates that even high dosages of lime (200 mg/L) may be ineffective at removing some DBP precursors, especially low molecular weight humic materials such as fulvic acid [ix]. Adsorption of fulvic acid to $CaCO_3$ precipitates during the softening process is low, primarily due to electrostatic repulsion arising from the high negative charge density of fulvic acid and the negatively charged $CaCO_3$ surface. In addition,

$CaCO_3$ particles formed during softening have low surface area (5 m^2/g) and therefore minimal sites for humic adsorption, compared to other coagulants such as ferric chloride (230 m^2/g). While the formation of $Mg(OH)_2$ during softening can aid in removing DBP precursors, the precipitation of magnesium occurs only at high pH, a condition uncommon in most water treatment plants [x].

In this research, we are investigating means to increase the removal of DBP precursors during lime soda softening. In particular, we are examining whether the adsorption of humic and fulvic acids to $CaCO_3$ precipitates during lime softening can be significantly improved through the "co-adsorption" of synthetic polymers. By co-adsorption, we mean any process by which more than one type of polymer simultaneously or sequentially adsorb to a solid surface. We believe the affinity of disinfection by-product precursors for calcium carbonate precipitates can be increased significantly through co-adsorption, and in particular, by the formation of humic-polymer complexes and/or through the attachment of humic material to polymer-coated $CaCO_3$ surfaces.

Specific objectives of this research include; (1) To examine the removal of DBP precursors by lime softening in the presence of a number of different synthetic polymers. (2) To determine the properties of organic matter and synthetic polymer (e.g., molecular weight, charge, hydrophobicity) that influence DBP precursor removal during co-adsorption. (3) To identify the importance of specific co-adsorption mechanisms that influence organic matter removal during softening, such as precipitate surface modification and organic matter/polymer interactions. Furthermore, a significant component of this work involves the transfer of information to scientists and engineers working in the water treatment field, regulators, and to other water treatment professionals.

Methodolody :-(Results to Date -Project Startup)

A Ph.D. student in the Department of Civil and Environmental Engineering and Geodetic Science, Mr. Mustafa Bob, is currently assigned to the project. Mr. Bob began working on the project on January 1, 1999. Mr. Bob recently completed his M.S. degree in Environmental Engineering and therefore has a good background for the current project. In addition to assigning a student to the project, supplies and equipment have been purchased including calcium carbonate particles, miscellaneous reagents, and glassware. Polymeric additives have been purchased from Polydyne Inc. Humic substances have been obtained from two sources: Aldrich Chemical Corporation and the International Humic Substances Society (IHSS). IHSS humic substances have been extensively characterized previously. The size and hydrophobicity of Aldrich humic acid has been examined in our laboratory using ultrafiltration and UV measurements, respectively.

Adsorption Experiments- The adsorption of humic acid onto model $CaCO_3$ particles is currently being examined in batch experiments. The purpose of these experiments is to ascertain the factors controlling the adsorption of humic substances to $CaCO_3$ particles in a model system. These experiments will help elucidate the mechanisms controlling the adsorption of humic *materials under different conditions, information important in developing strategies for increasing humic adsorption.*

To carry out an adsorption experiment, humic acid is diluted into carbonate buffer, $CaCO_3$ particles are added, and then the mixture is incubated for at least 2 hours at 23 °C. Control experiments are carried out to verify that the amount adsorbed does not change significantly after the 2 hour incubation period. The pH at the beginning of each adsorption experiment is adjusted to either 7 or 9 using either 0.1 M HCl. The particles are allowed to reach equilibrium with respect to pH prior to conducting an adsorption measurement. No significant change in pH has been observed over the course of an adsorption experiment. After incubation, the $CaCO_3$ particles are separated from the liquid phase by filtration through sterile 0.1 □m pore size Millex disposable filters (Millipore, Bedford, MA). Control tubes containing humic acid and no $CaCO_3$ particles are treated in an identical manner. In no case has any significant removal of organic matter onto filter media been observed, and therefore, the measured change in organic matter concentration is due solely to adsorption to the surface of the $CaCO_3$ particles. In addition, it has been verified that the filtration step removes all measurable amounts of $CaCO_3$ particles from suspension. The fluid concentration of organic matter, before and after exposure to $CaCO_3$ particles, is determined by measuring total organic carbon (TOC) using a total organic carbon analyzer (TOC5000, Shimadzu Scientific Instruments, MD). The adsorbed amount is calculated by measuring the depletion of organic matter in solution.

Principal Findings and Significance: The data in Figure 1 show the adsorption of humic acid to calcium carbonate particles at two different pH values: 7.5 and 9.5. As can be seen, adsorption of humic acid is significantly greater at pH 7.5 as compared to pH 9.5. Preliminary data suggest that the greater adsorption at low pH is due to the lower negative surface charge of the particles at pH 7.5 as compared to pH 9.5. The data also suggest that humic acid has a high affinity for the particles at low equilibrium concentrations, however, the amount adsorbed reaches a maximum upon saturation of the $CaCO_3$ surface. Preliminary measurements with cationic polyelectrolytes suggest that coating the $CaCO_3$ particles with a positively charged polymer at pH 9.5 (the typical pH in water softening plants) greatly increases the amount of humic acid adsorption.

Future Work-Future work will focus on further examining the effect of polymeric additives on the adsorption of humic substances to $CaCO_3$ particles. In particular, we are currently examining the influence of humic acid chemical composition, polymer size and charge, pH, ionic strength, and $CaCO_3$ surface properties (electrostatic potential, surface area, minerology) on humic acid adsorption. Our main goals in these experiments are to elucidate the mechanisms controlling the adsorption process and determine optimum conditions for organic matter adsorption during polymer-assisted softening.

We also plan to examine the influence of polymeric additives on the structure of $CaCO_3$ flocs. Floc structure will determine the settling characteristics of $CaCO_3$ particles and therefore will significantly effect the removal of organic matter during softening in large-scale operations. To examine floc structure we will measure the coagulation kinetics of $CaCO_3$ particles by monitoring the change in the mean size of suspensions using a photon correlation spectrometer. We will also directly examine floc structure by transmission electron microscopy.

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SYNOPSIS

Project Number: C-09 | Start Date: 09/98
End Date: 08/00

Title: In-situ Destruction of Solvents by Permanganate Oxidation

Investigators: Franklin W. Schwartz, The Ohio State University

Congressional District: 15th

Focus Category: GW, TS, HYDGEO

Descriptors: groundwater, DNAPL, in-situ remediation, oxidation, potassium permanganate

Problem and research objectives: The contamination problems posed by chlorinated solvents are well known. When dissolved in contaminant plumes, chlorinated solvents pose an extremely difficult challenge for hydrogeologists attempting to remove them from the subsurface. First, even low aqueous concentrations could be greatly in excess of the public drinking-water standards, although many chlorinated solvents are sparingly soluble in water. Thus, a large volume of groundwater can be contaminated by a small volume of spilled solvent. Secondly, due to their stability and persistence in the subsurface, pools and residual solvents can remain over many decades, or even centuries and serve as a long-term source of continued groundwater contamination. Finally, chlorinated solvents typically do not move along the flow gradient in aquifers because they are denser than water and tend to move downward under a separate hydraulic head.

Industries and government agencies alike have an important stake in research related to the clean up of chlorinated solvents at contaminated sites. Many severely contaminated sited remain to be cleaned up in the United States and around the world. The main motivation for research on alternative technologies is that some conventional schemes (like pump-and-treat or in situ bioremediation) have limitations in dealing with solvent contamination. For example, the undetected presence of DNAPL at a site generally relegates pump-and-treat schemes to an effort in hydraulic plume control rather than mass recovery. Bioremediation schemes have been difficult to implement. Potential problems or limitations of such approaches involve metabolite toxicity, competitive cosubstrate inhibition, and difficulties in process optimization for aerobic conditions.

Thus, formidable challenges remain in developing schemes for the clean up of DNAPL sites. other conventional approaches like soil vapor extraction and gas sparging work well when site conditions are appropriate. There remains a need for research to develop approaches to treat contaminants due to both free phase and dissolved solvents.

Problem and Research Objectives

The contamination problems posed by chlorinated solvents, like PCE, TCE and DCE, are well known. When dissolved in contaminant plumes or present as DNAPLs, solvents pose an extremely difficult challenge in cleanup. A few studies (e.g., Schnarr et al., 1998) have explored the efficacy of using oxidants, in particular potassium permanganate to destroy solvents present as a dissolved phase in aqueous solutions. The obvious advantages of the method include cost, the relatively benign character of the intermediates and the fast kinetics of the oxidation reactions. Our group for the past several years has undertaken fundamental studies to explore the potential reaction pathways and kinetics (Yan, 1998). Given the very positive outcome of these experiments, we propose to take the next logical step in the development of this methodology and move from small-scale batch and column tests to more realistic large-tank tests. The objectives of the proposed study are:

(i) to undertake proof-of-concept studies to determine the efficacy of DNAPL removal in large scale flooding schemes,
(ii) to elucidate how the efficiency of DNAPL removal is influenced by (a) flow by-passing due to multi-phase effects, (b) the presence of MnO_2, and CO_2, which form in the overall reaction, and (c) the design of the flooding scheme, and
(iii) to develop further promising electrical and optical monitoring schemes from previous studies.

Methodology

The proposed study will involve experiments to be conducted in a large plastic flow tank (approximate dimensions 2x3x6 ft) lined with solvent-resistant Plexiglas. Overall, the experiments will involve three different patterns with heterogeneity in hydraulic conductivity. The heterogeneity will provide for realistic flushing schemes and avoid simply having the DNAPL pool at the bottom of the tank. The heterogeneous media will be constructed by carefully placing volumes of various sand and silt fractions into the tank in a known arrangement. Final specifications for each arrangement will be developed from column experiments designed to characterize the vertical migration of DNAPLs with various media. However, we anticipate that one medium will involve many thin layers, a second would involve a smaller number of somewhat thicker layers and the third would be constructed with less continuous lenses of higher and lower hydraulic conductivity.

The flow tank will be operated to provide an ambient flow. A treatment zone will be located in a central portion of the tank. As a preliminary to the DNAPL experiment with each one of the three, we will undertake tests of flushing efficiency using different arrangements of injection and withdrawal wells – both horizontal and vertical arrangements. We can determine how efficiently zones between the wells would be flushed by a permanganate solution. We know from previous studies (e.g., Schincariol et al., 1993; Swartz and Schwartz, 1998) that fluid density differences will cause complex patterns of mixing with horizontal displacements. It is possible that taking advantage of density differences with vertical arrangements could improve the spreading of potassium permanganate. This testing approach will let us conduct a variety of useful experiments without replacing the medium after each experiment.

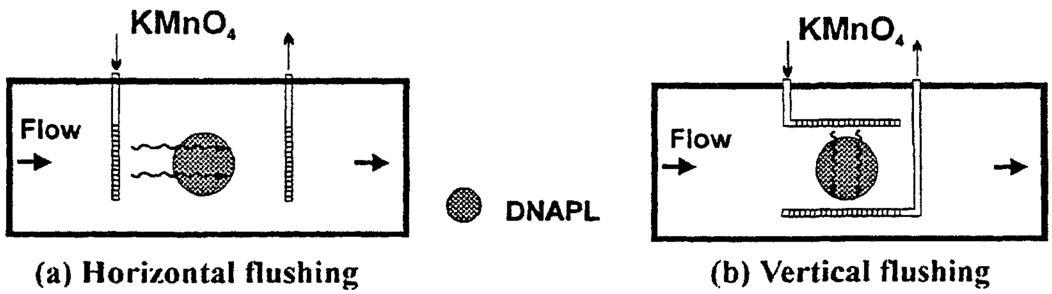

Figure 1. Schematic diagram of in-situ horizontal (a) and vertical (b) flushing.

The actual experiments with TCE will involve injecting the dyed liquid slowly through standpipes emplaced in the upper portion of the tank. It will be possible to characterize the initial distribution of product using both visual and optical approaches that are outlined in a following section. The study requires detailed monitoring of the mass transport and mass transfer reactions. A dense network of glass mini-wells will be provided to collect fluid samples as experiments progress and to measure hydraulic conductivity values in situ. In addition, we propose to monitor both the flushing-efficiency experiments, and the TCE oxidation experiments both electrically and optically.

Principal Findings and Significance

A student, Y.C. Fang has been recruited to work on the project as part of his Ph.D. dissertation. Mr Fang has a bachelors degree in civil engineering and a M.S in statistics. To date, work on this project has involved the construction and leak testing of the flow tank and the development of optical and electrical monitoring systems. Logistically, this has been more difficult than anticipated because it has been necessary to deal with leaks from the tank, and to find materials that would be unaffected by TCE. Figure 2 is a photograph of the (2x3x6 ft) tank mounted on a wooden dolly for mobility. A chemically resistant liner has been added to keep the tank water tight.

Figure 3 is an example of the monitoring wells to be installed in the tank. The wire is gold-coated to avoid interaction with the TCE in pure and dissolved phases. The necessary soldering and circuit connections have been completed. We are presently within a few days of beginning to fill the tank for the first experimental trial.

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Figure 2: Photograph of the flow tank on the wheeled dolly.

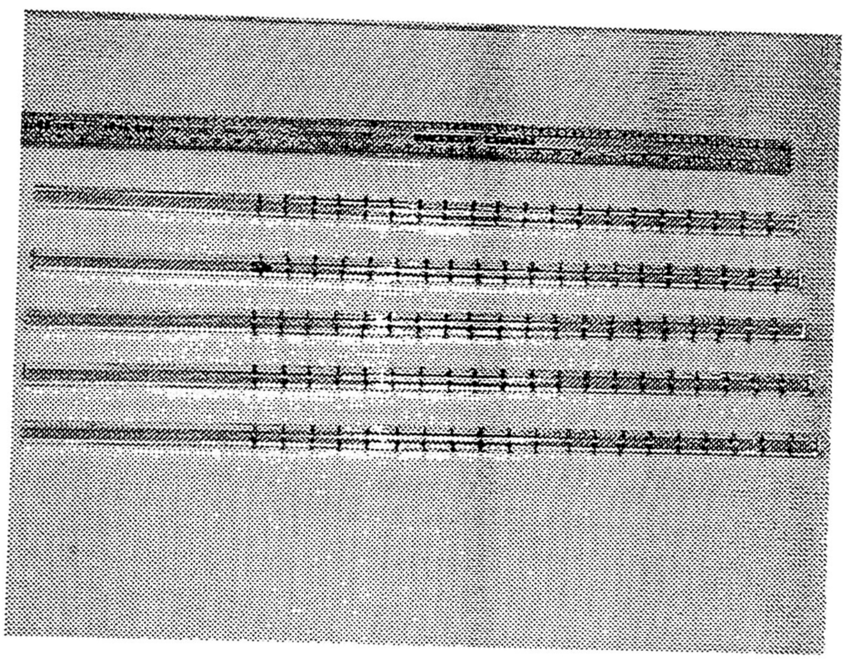

Figure 3: Flow tubes used for electrical/optical monitoring.

SYNOPSIS

Project Number: C-10 Start: September, 1998
End: August, 2000

Title: Nutrient Cycling in Integrated Cropland/Wetland/Reservoir Management Systems

Investigators:
Larry C. Brown, Dept. Food, Agric., and Biol. Engr., The Ohio State University
Scott Subler, Formerly - Dept. Entomology, The Ohio State University
Norman R. Fausey, USDA-ARS Soil Drainage Res. Unit, Columbus

Congressional District: OH 15

Focus Categories: AG, WL, NU

Descriptors: Agroecosystems, nutrient cycling, constructed wetlands, drainage management, nitrogen, phosphorus, organic carbon, nutrient delivery to streams, sediment, runoff, subsurface drainage, controlled drainage, subirrigation, ecosystem models, Great Lakes, water reuse and recycling, landscape and watershed management, off-site impacts.

Problem and research objectives:

The Midwestern US comprises the most productive agricultural region in the world. The predominant agricultural management systems in this region receive extensive nutrient inputs. However, most of these management systems do not effectively utilize or retain all of the added nutrients, leading to growing problems with nonpoint source contamination of surface and ground waters. Some of these problems may be exacerbated by traditional technologies for managing soil water. In many parts of the Midwest, soil drainage, the removal of excess water from the surface and profile of cropland soils by either gravity or artificial means, is an indispensable agricultural practice. In areas such as northwestern Ohio, once known as the "Great Black Swamp," water management practices are critically important for continued prosperous agriculture, the quality of Lake Erie water, the local economy, and for the restoration and preservation of wildlife habitat areas. Landowners there are encouraged to utilize technologies for surface drainage, subsurface drainage, and best management practices necessary for sustained agricultural performance and improved water quality. Nevertheless, the quality of Lake Erie water is still affected by nonpoint source agricultural runoff, and is substantially impaired by current cropping management practices combined with traditional, but effective, surface and subsurface water management techniques. Influxes of sediment, nitrogen, phosphorus, and agricultural chemicals are the greatest environmental concerns.

Ironically, when the original wetlands were converted to productive cropland through the installation of drainage systems, the ecological capacity of the landscape to filter sediment, retain nutrients, and purify surface water arising from the new agricultural land was lost. Inventory data indicate that 22 states have lost 50% or more of their original wetlands. In the North Central Region's dominant drainage states of Ohio, Iowa, Indiana and Illinois, over 85% of the original wetland acreage has been lost.

Within the eight-county Maumee Valley Resource Conservation and Development Area (RC&D), total wetland loss is estimated at 122,555 acres. Loss of wetlands, as associated with declines in wildlife habitat, adverse effects on water quality, and other impairment of healthy ecosystem function, is an important environmental issue. In typical farming communities of northwest Ohio, 80–90% of all land use is agricultural. Voluntary restoration of wetlands in this area has been minimal, largely due to tradition and economic considerations. For successful adoption by landowners, wetland development must make sense within an agricultural context, and must be cost-effective in the absence of government subsidies.

Progressive farmers and their organizations, natural resource conservation agencies, environmental agencies and organizations, and others seek guidance to help society and agriculture better understand how to recreate valuable wetlands, while conserving our existing beneficial wetlands. The development and demonstration of integrated landscape management systems, which combine the productive functions of cropland and improved water use with the ecological functions of wetlands and reservoirs, offer great promise. Exciting and innovative new projects are currently underway to evaluate the management, hydrology, and economics of such cropland/wetland/reservoir (C/W/R) systems. However, critically important questions concerning nutrient cycling through these systems, and their ultimate impacts on water quality, remain to be addressed.

There is increasing awareness and excitement about the potential for integrating diverse ecosystem types within a landscape to provide environmental benefits while sustaining agricultural production. Although numerous research programs currently address the potential component functions of particular ecosystems (for example, the 'filtering' capacity of wetlands or riparian strips), very few have attempted to develop truly integrated landscape management systems. One such system, recently implemented in Ohio, combines crop, wetland, and reservoir ecosystems in an innovative closed-loop design by which water and nutrients are recycled within a farm. This innovative, ecologically-sound production system has the potential to greatly reduce the discharge of sediments and agricultural chemicals to streams and improve water quality, to increase wetland area and wildlife habitat, and to recycle water and nutrients for improved crop production and enhanced farm profitability.

We are investigating and modeling nutrient cycling dynamics and related water quality impacts of newly developed integrated cropland/wetland/reservoir (C/W/R) landscape management systems in Ohio. Three operational C/W/R landscape management systems function as partially closed loops, through which water and nutrients are recycled among individual component ecosystems (cropland, wetland, water supply reservoir). In these systems, runoff and drainage from cropland is collected and directed through a constructed wetland, and then stored in an on-farm reservoir. During the crop season, the cropland is subirrigated by supplying water from the reservoir back through the subsurface drainage lines beneath the crops. These systems use appropriate, state-of-the-art water table management technologies to achieve goals of improved water quality, increased wetland acres and biodiversity, and enhanced farm profitability.

This work builds on established research, demonstration, and education projects in Ohio, and we will provide critical information on the cycling and transport of nutrients in cropland/wetland/reservoir management systems. This work does not duplicate, but builds upon a substantial infrastructure provided by two existing projects that 1) demonstrate construction and management (funded by USEPA et al.), and 2) evaluate hydrology and economics of C/W/R systems for corn and soybean production on field-sized areas (*Economic and Hydrologic Analysis of Integrated Wetland-Reservoir and Subirrigated Agricultural Production Systems*, Brown and Batte, funded by WRRI in 1997).

Funds from USEPA are currently being used to demonstrate the construction and management of cropland/wetland/reservoir systems at three sites in Ohio. The existing demonstration project funded by USEPA/GLNPO demonstrates construction and management of permanent wetland/reservoirs linked directly to subirrigated corn and soybean production systems on field-sized areas in the Maumee River basin in Ohio. The demonstration project is managed by a team of farmers, local, state and federal agency personnel, university faculty, the drainage industry, and others, including Dr. Brown and Dr. Fausey (Co-PIs on the new work). The construction, management, and instrumentation phases are fully funded. Three systems are fully operational. Each site has a subirrigated C/W/R system area, and a conventionally subsurface drained (not subirrigated) comparison area. Each site offers some unique characteristics that, when combined over all three sites, allow excellent research opportunities over a range of conditions.

Research funded in 1997 by WRRI (Brown and Batte) is evaluating the hydrology and economics of these systems. For the research on <u>hydrology and economics</u> of these systems, the objectives are: 1) to characterize, analyze, and model hydrologic interactions in subirrigated cropland/wetland/reservoir systems, 2) to evaluate farm-level economics of these systems, and 3) to develop a technical design and system management guide for these systems, and to conduct an applications and design workshop to teach agricultural producers and consultants how to use water table management for environmental and economic benefits.

This new work adds a missing, yet essential, component of research (nutrient cycling) to the evaluation of the functioning and environmental impacts of these systems. The new project takes advantage of this existing research program, and extends it to include detailed characterization and preliminary modeling of nutrient stocks and flows within and among the component ecosystems of the C/W/R management system. Such an ecosystem analysis is critically essential for understanding the functioning and potential environmental impacts of these systems. The specific objectives of the new project are stated below, each with a summary statement.

Research Objectives

Objective 1: To quantify the cycling and transport of nutrients (soluble and sediment bound) within and between the ecosystem components of existing cropland/wetland/reservoir landscape management systems.

We have begun to collect hydrologic and economic data from three C/W/R management systems (all three systems are managed by farmers). However, detailed information on nutrient cycling is lacking. Assessing inputs, storage, and outputs of critical nutrients, such as nitrogen, carbon, and phosphorus, and interactions with sediments for each component ecosystem, as well as for the whole system, is essential for understanding system function and for evaluating potential water quality and crop production benefits. We are building upon our success in a related project in southern Ohio where we recently developed system level nitrogen budgets for a subirrigated/controlled drainage system, a central component of the C/W/R landscape management system.

Objective 2: To initiate the development of a preliminary system-level model of nutrient flows and recycling for cropland/wetland/reservoir landscape management systems.

Data on nutrient stocks and flows generated from the first objective will allow us to initiate the construction of preliminary system-level models of nutrient cycling. Coupled with hydrologic models currently being developed for the system, these models will eventually aid in understanding overall system function, and will allow us to evaluate different management scenarios in a future stage of the project. Such models can also be powerful tools for communicating principles of system design and operation to engineers, natural resources managers and technicians, farmers, and other end-users. Clearly, the market for these technologies is well established.

Methodology:

Overall Approach

he overall approach is an ecosystems analysis of nutrient stocks and flows within and among each of the components of the C/W/R system. Over the funded study period, quarterly estimates will be made of total ecosystem nutrient stocks (C, N, P), and nutrient and sediment inflows and outflows will be measured on a continuous basis with automated sampling equipment (equipment is funded). This information will be used to intitate the preliminary construction of simulation models that will allows us eventually to assess system function and water quality impacts over a range of management scenarios.

Existing Funded Demonstration Project

The new research is focusing on three constructed and operational sites: Defiance Agricultural Research Association (DARA) site (near Defiance County airport and weather station); Fred Shininger farm (Fulton County); and Marsh Foundation (Van Wert County, Farm Focus Site). The most intensive research and evaluation will be conducted at the DARA site. Each site consists of a subirrigated area for corn and soybean production, a constructed wetland, and a constructed upground reservoir (or existing pond). Runoff and subsurface discharges from adjacent cropland are routed to the constructed wetland. Water from the wetland is pumped to the upground reservoir where it is stored for water supply. During the crop season, water is pumped into the subirrigated cropland, where a water table is held at a 14- to 20-inch depth throughout most of the growing season. Each site has numerous locations to measure and sample surface and subsurface flows, subirrigation water use, runoff, etc. The DARA site is currently being instrumented so that water flow rates and volumes can be measured, and sediment and water samples can be collected for each component of this integrated system. Complete details of the currently funded components are summarized by Brown and Batte's WRRI project.

<u>Approach for Objective 1</u>: To quantify the cycling and transport of nutrients (soluble and sediment bound) within and between the ecosystem components of existing cropland/wetland/reservoir landscape management systems.

Total stocks of carbon, nitrogen, and phosphorus will be estimated for each component ecosystem at least 4 times per year. The first sampling event was initiated in June 1999. In the crop systems, estimates will be based on soil and vegetation samples; in the constructed wetlands, on soil/sediment, water, and vegetation samples; and in the reservoirs, on sediment and water samples. Soil samples will be taken in the crop systems to the depth of the drainage tiles (approx. 75 cm) using a soil probe, separated into 0-15 cm and 15-75 cm depths, and analyzed at the Ohio State University Soil Ecology Laboratory for total and available C, N, and P. Total nutrient contents in the soil profile will be determined one time each year, as they are unlikely to change significantly during this time. However, available (extractable) concentrations of C, N, and P are likely to be much more dynamic, and represent a large fraction of the mobile nutrients that are available for crop uptake, transport between compartments, or loss from the system; concentrations of nitrate, ammonium, phosphate, and dissolved organic C, N and P will be determined four times a year (early spring, after fertilization, at harvest, mid-winter).

In the wetland, soil sampling will be conducted similarly, except that cores will only be taken to the effective rooting depth of the aquatic vegetation, and samples of deposited sediments will be taken separately. In the cropland and wetland systems, vegetation samples will be taken twice annually (spring and fall) to allow estimates of standing stocks and uptake of nutrients during the growing season. Water samples from the wetlands and reservoirs will be taken, on an hourly to a weekly basis depending upon rainfall and runoff events, using standard sampling bottles and techniques. Additional water samples to meet the specific needs of the proposed work will be also taken.

Total C and N concentrations in soil, sediment and vegetation samples will be determined using a Carlo-Erba C/N analyzer, total P will be determined colorimetrically following acid digestion. Nitrate, ammonium, and phosphate in extracts and water samples will be determined colorimetrically using microplate methods; dissolved organic carbon will be determined using a Dohrmann TOC/DOC analyzer, and dissolved organic N and P will be determined colorimetrically following persulfate digestion of liquid samples.

Monitoring of water levels and flows from each system compartment will be conducted as a part of the currently funded WRRI project. Runoff and subsurface discharge will be monitored and evaluated before, during and after selected storm events (hopefully 10 to 20 storm events annually), and during selected less-dynamics times throughout the year. One-liter water samples will be collected during flow events. All samples required for the proposed project will be analyzed for nitrate and soluble phosphorus, and for dissolved organic C, N, and P at OSU's Soil Ecology Laboratory and Environmental Chemistry Laboratory. All concentration data will be analyzed on a flow-weighted basis. Sediment samples will be analyzed locally by gravimetric means, and for total C, N, and P contents. Sedimentation rates are already being assessed seasonally and annually. Inflows and outflows from each flow control point will be measured at the time of sampling using automatic flow rate and volume measurement devices (already funded). Rainfall at each site will be measured using manually read rain gauges; a weather station is being installed at the DARA site (funded), and local weather records are available in each county.

Crop growth and production characteristics will be measured during each crop season. Crop yield, crop production management, tillage, and nutrient and pesticide application data will be collected from each cooperator. This will allow estimation of total nutrient imports and exports to the crop system through fertilizer inputs and harvested grain. Estimates of respiratory losses of carbon and inputs of nitrogen through fixation by the soybean crops will be based on literature values for comparable cropping systems; estimates of losses of nitrogen through denitrification from the crop systems and wetlands will be based on literature values and on results of plot-level research on other subirrigated systems in Ohio currently being conducted by the PIs.

<u>Approach for Objective 2</u>: To initiate the development of a preliminary system-level model of nutrient flows and recycling for cropland/wetland/reservoir landscape management systems.

We have begun the identification and evaluation of several system-level budget and ecological simulation models. Eventually, we will possibly modify one or more of these models using our data on nutrient stocks and flows from the component ecosystems, as well as our data from the southern Ohio research. We have had great success developing system-level nitrogen budgets for subirrigation/controlled drainage systems in poorly drained soils in southern Ohio. Initially, sediment, carbon, nitrogen, and phosphorus transport at the DARA site will be evaluated using our preliminary simple compartmentalized dynamic simulation models. We eventually hope (with future funding) to evaluate these models linked with more elaborate mechanistic models requiring detailed inputs on soil characteristics, cropping system, meteorological data, etc, collected from the DARA site and then from the other two sites.

In conjunction with hydrologic management simulation modeling work (funded), these preliminary system-level models could be used to conduct computer simulations based on long-term climatic records and different management scenarios to evaluate the nutrient recycling and crop production potential of C/W/R systems under various scenarios and at different locations throughout the Midwest. Currently, DRAINMOD-N, ADAPT (Agricultural Drainage and Pesticide Transport), and GLEAMS are three such models that have the capability to model nutrient cycling and water table management scenarios. For the funded WRRI project (Brown and Batte) ADAPT will be used to model erosional processes and nitrogen and phosphorus transformations and transport (based upon algorithms adapted from GLEAMS). Because of its wider acceptance throughout the US to evaluate the hydrology of agricultural land use areas and wetland hydrology, and its relatively new nitrogen component, DRAINMOD-N will be used in addition to ADAPT. For conditions at all sites, our expected results from the proposed project on nutrient cycling will easily feed into, and enhance predictions from the funded, long-term simulation work that will be used to develop matrices of crop yield, nitrogen and phosphorus transport relationships.

Technology Transfer Objective (taken from Brown and Batte, found elsewhere in this report): Develop a technical design and management guide for subirrigated agricultural production and constructed wetland-reservoir systems, and conduct an applications and design workshop to teach agricultural producers and consultants how to use water table management for environmental and economic benefit.

Although the technology transfer objective was not explicitly stated in the new project proposal, the new work is very strongly connected to the overall project, and thus to the technology transfer objective. All research and demonstration results will feed into management guide development, with a primary focus on environmental and economic benefits of water table management and constructed wetlands, site identification, water supply, engineering design, construction, and system operation and management. All aspects of the overall project feed into Dr. Brown's educational activities conducted cooperatively by Ohio State University Extension, the demonstration project and its cooperators and technical advisors, and the Overholt Drainage Education and Research Program at The Ohio State University. Outreach is also linked to activities of the new regional NCR Project 195 "Mississippi River

Watershed Nutrient Sources and Control." Previously, Brown and Batte predicted that results from all components of the overall project would have implementation implications for the entire Midwest, and within the past year researchers and technical agency personnel from across the Midwest have expressed an interest in developing a new future project with a comprehensive regional application of this technology.
Progress report:

One Ph.D. student joined the project in January 1999, and one M.S. student joined the project in April 1999, both in the University's Environmental Science Graduate Program. The field sampling schedule has been developed and initial laboratory analysis is underway. In December 1998, Dr. Subler joined a consulting firm in Washington State, but he maintains a strong linkage to the project.

Prior to WRRI funding, three constructed wetlands were designed, constructed, and linked with water supply reservoirs for corn and soybean production systems using subirrigation. All three systems, located in the Ohio portion of the Maumee River Basin, were operational in the 1997 and 1998 growing seasons, and provided yield data. The wetlands were constructed on prior-converted cropland (soils dominantly silty clay) to receive drainage from adjacent cropland, resulting potentially in zero-discharge from cropland directly to streams, except during extreme precipitation events. Agricultural runoff and subsurface drainage recharge the wetland seasonally, and the reservoir serves as a supplemental water supply source for subirrigating corn and soybean. The constructed wetlands, primarily designed to serve as runoff and drainage collection and detention components, have developed wetland vegetation. A comprehensive monitoring system has been designed for the Defiance County site, and is now being completed. We are now able to collect a large variety of data useful for hydrologists, biologists, wetland ecologists, modelers and decision support system designers, engineers, and natural resources conservationists. A summary of individual subprojects within the overall research scope (Brown and Batte) is provided elsewhere in this report.

Results from this research will help characterize ecological processes and management factors that influence transport and storage of nutrients in and out of integrated cropland/wetland/reservoir landscape management systems. Ultimately we will use our results to develop an assessment of the actual reduction of plant nutrients normally lost to receiving waters, establish the potential benefits/impact of these systems on nutrient fate at a local level, and subsequently forecast to a small watershed scale. Our expected results will certainly extend well beyond those to be determined by the existing WRRI research of Brown and Batte (see elsewhere in this report). Our research is very important for building a foundation for future GIS/remote sensing and watershed modeling research that can evaluate various application scenarios and predict environmental impacts on watershed and regional scales.

The project enjoys great interdisciplinary, multi-agency, and stakeholder participation. The overall project is a cooperative team effort between the Maumee Valley RC&D (MVRC&D), USDA-Natural Resources Conservation Service (NRCS), USDA-Agricultural Research Service (ARS) Soil Drainage Research Unit, The Ohio

State University (OSU), Michigan State University (MSU), Heidelberg College (HC), University of Findlay, Soil and Water Conservation Districts (SWCD), farm cooperators and county commissioners, Ohio and Michigan Land Improvement Contractors (O&MLICA), Drainage Products Industry (ADS, Hancor, Haviland, Baughman), ODNR Division of Wildlife (SW), USF&WS, USACOE, and other local and state agencies and organizations.

The overall project funding is provided, in part, by USEPA GLNPO; Lake Erie Protection Fund; OARDC and OSU Extension; Ohio Sea Grant College Program; USGS Water Resources Competitive Grants Program; Water Resources Center, The Ohio State University; USDA-ARS Soil Drainage Research Unit; USDA-CSREES Hatch Proj. 965; Overholt Drainage Education and Research Program, Dept. Food, Agric., and Biol. Engr., The Ohio State University; and the cooperating landowners, agencies and organizations.

This innovative, ecologically sound crop production system will recycle runoff and drainage waters, reduce runoff, sediment, and agricultural chemical discharges to streams, improve water quality, increase wildlife habitat, increase wetland acres, and enhance farm profitability. The demonstration project team (farmers, state and federal agency personnel, university faculty) will provide high level input to proposed research and help evaluate application of results to users. Integrated research and demonstration efforts will produce a management guide with focus on environmental and economic benefits, site identification, water supply, engineering design, construction, and system operation and management.

<u>Related research:</u>

Although numerous research programs currently address the potential component functions of particular ecosystems (for example, 'filtering' capacity of wetlands or riparian strips), very few have attempted to develop truly integrated landscape management systems.

It is clear that agricultural water management is a critically essential element of agricultural production in much of the Midwest, and that agricultural drainage does have both beneficial and adverse impacts on water resources. The eight Corn Belt and Great Lakes states account for nearly 80% of U.S. agricultural production. Over 20.6 million ha of agricultural land are presently under artificial drainage. Research from across the Midwest indicates that conventional agricultural drainage practices can provide both positive and adverse impacts on surface water resources (Fausey et al., 1995). Skaggs et al. (1995) cite studies from the US, Canada, Europe and elsewhere that indicate that improved drainage and agricultural production usually increases peak runoff rates, sediment losses, and pollutant loads on surface water resources, compared to uncleared land. Subsurface drainage practices may increase the loss of some pollutants (i.e., nitrate) and decreased the loss of others (sediment, phosphorus, some pesticides). Before 1985, with the exception of work conducted in North Carolina, little attention was given to the proper management of existing subsurface drainage systems and the subsequent impact on water resources for both a quality and quantity standpoint. Subsurface drainage systems drain near-surface perched water tables. These drainage systems actually provide the opportunity to detect some water quality problems, and then possibly control or eliminate these problems by: 1) diverting excess subsurface water that contains potential pollutants to a treatment system; 2) controlling the water table to promote biological and chemical degradation of potential pollutants; and/or 3) controlling the timing of release of drainage water to surface- and ground-water bodies to minimize environmental impact (Brown et al., 1998).

Previous research has indicated that nitrate concentration in drainage water could be reduced by enhancing denitrification (Davenport et al., 1975; Evans and Skaggs, 1989; Skaggs and Gilliam, 1981; Willardson et al., 1972). Madramootoo et al. (1993) showed that a controlled water table as shallow as 40 cm from the surface could decrease nitrate in the soil profile by up to 50%. Kimmelshue et al. (1995) indicated the possibility of enhancing denitrification by establishing high water table depth and concluded that water table control could be used during the winter to promote denitrification, thus minimizing nitrate lost to drainage water. In a 1995 issue of the Journal of Irrigation and Drainage Engineering, drainage researchers from across the U.S. summarized the state of our knowledge about agricultural drainage and water quality, and documented the potential for water table management (WTM) to help reduce adverse water quality impacts (i.e., Backlund et al., 1995; Evans et al., 1995; Fausey et al., 1995; Ritter et al., 1995; Shirmohammadi et al., 1995; Thomas et al., 1995). A new regional bulletin (Zucker and Brown, 1998), developed by the regional Management Systems Evaluation Area Projects in Ohio, Minnesota, and Iowa, with contributions from Michigan, Illinois and Indiana, has completed a comprehensive documentation of such impacts.

However, we know that nitrate losses through drainage systems to surface water resources is a fact, and that phosphorus losses are decreased with proper water management, but we do not fully understand the dynamics of nutrient cycling in these systems. In general, agroecosystem properties and processes that interact with soil hydrology, climate and other site conditions to determine the net loss or retention of nutrients are complex and are only very poorly understood.

Water table management to reduce the impact of agricultural production on surface and subsurface water quality has not been fully evaluated in the Midwest. However, experience in the coastal plain region of the southeastern US, and recent efforts in the Saginaw Bay area of Michigan, strongly suggest a reduction in excessive nitrate-nitrogen discharges may be accomplished by managing subsurface drainage water in conjunction with other acceptable best management practices (soil testing, split fertilizer applications, etc.). By removing excess water through drainage early in the growing season, and subirrigating through tile lines during the growing season to avoid drought stress, water table management may promote the efficient use of applied nutrients and enhanced crop productivity. Our research on subirrigation in Ohio indicates that water table management can result in more predictable yields, allowing more efficient use of applied agricultural chemicals, and less opportunity for water

quality problems to develop. Maintenance of a constant, shallow water table during the growing season by use of a subirrigation/drainage system can improve water quality; and when combined with a high yield crop management system, can result in average soybean yields of 0.08 to 0.09 metric ton/ha (70 to 80 bu/ac) and average corn yields of 0.21 to 0.22 metric tons/ha (190 to 200 bu/ac).
We recently developed system-level nitrogen budgets for subirrigation/controlled drainage systems in poorly drained soils in southern Ohio. We measured soil storage of nitrogen and system outputs of nitrogen through grain harvests, runoff, drainage outflow, and denitrification and compared them with those of conventionally subsurface drained systems. Denitrification losses of N were greater in the subirrigated/controlled drainage system than in the subsurface drainage system. Grain yields and nitrogen uptake were also significantly greater in the subirrigated/controlled drainage system. In soil beneath the rooting zone, end-of-season mineral nitrogen concentrations were reduced in the subirrigated/controlled drainage system compared to the subsurface drainage system (suggesting a reduced potential for drainage losses of nitrogen). Although data on the total losses of nitrogen through drainage outflows and surface runoff are currently being analyzed, the preliminary results suggest that subirrigated/controlled drainage systems may reduce the nitrate contamination of surface waters, primarily through increased crop uptake of applied N, compared to conventional subsurface drainage systems.

Recent studies have estimated either farm-level N budgets or large watershed N sources and flows to evaluate nutrient (primarily nitrate) inputs to surface water resources. Walker et al. (1998) determined field sources, transport, and river export of nitrate from an agricultural watershed. Agricultural field N sources and sinks, tile drainage nitrate concentrations and fluxes, and river nitrate export were estimated for an entire watershed. On average, nearly half of the inorganic nitrogen pool in the field soil was leached through drainage systems and seepage, and then exported to the river. It was concluded that agricultural disturbance (high mineralization inputs of N) and N fertilization, combined with tile drainage, contributed significantly to the nitrate export in the river. Other studies have coupled nutrient budgets of agricultural fields and riparian vegetation strips or wetlands to demonstrate the considerable nutrient retention capability of these ecosystems. However, in most of these studies water flow and nutrient transport is considered to be one way; few studies have attempted to link nutrient budgets of different ecosystem types within a integrated landscape management system that can recycle nutrients within the system, potentially increasing nutrient use efficiency and reducing nutrient export to surface water.

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Other Publications

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Agricultural Constructed Wetlands, and Wetland-Reservoir Subirrigation Systems. Designing Agricultural Systems to Balance Production and Environmental Objectives. Miscellaneous Bulletin OAWMGWP No. 3/3-1999. Food, Agricultural, and Biological Engineering Department, The Ohio State University.

Soil Properties Important for Drainage. Designing Agricultural Systems to Balance Production and Environmental Objectives. Miscellaneous Bulletin OAWMGWP No. 4/3-1999. Food, Agricultural, and Biological Engineering Department, The Ohio State University.

Soil Properties Important for Irrigation. Designing Agricultural Systems to Balance Production and Environmental Objectives. Miscellaneous Bulletin OAWMGWP No. 5/3-1999. Food, Agricultural, and Biological Engineering Department, The Ohio State University.

Presentations Scheduled:

L.C. Brown, N.R. Fausey, B.J. Czartoski, H.W. Belcher, J.A. Hothem, N.M. N'Jie, T. Oztekin, L. Luckeydoo, M.T. Batte, C. Davis, Fred, Marge, and Bill Shininger, P. Chester, B. Clevenger, L. Davis, P. Andre, D. Sutton. ____. Marketing Wetlands for Profit. Oral presentation, poster, and summary paper accepted for SWCS annual meeting.

L.C. Brown, N.R. Fausey, A.D. Ward, L.A. Zucker. ____. The Midwest Water Management ASEQ: Agricultural Drainage and Nitrate. (presentation and extended abstract for The Third National Workshop on Constructed Wetlands/BMPs for Nutrient Reduction and Coastal Water Protection, June 9-12, 1999, New Orleans, Louisiana).

Information Transfer Program:

In addition to the International professional meeting papers listed elsewhere, other presentations were made in 1998 on the overall project scope, demonstration, monitoring and research plans, and others are scheduled for 1999. See report by Brown and Batte.

Student Support:

Students

Undergraduate	2 (part-time; partial match)
Masters	1 (federal $ and partial match)
Ph.D.	1 (federal $ and partial match)
Post Ph.D.	0

Disciplines

Undergraduate	1 - Food, Agric., and Biol. Engr.
	1 - Environmental Sciences
Masters	1 - Environmental Sciences
Ph.D.	1 - Environmental Sciences
Post Ph.D.	0

D. Information Transfer Activities

The Water Resources Center administratively is part of the Department of Civil and Environmental Engineering and Geodetic Sciences and is physically located in the Agricultural Engineering Building at The Ohio State University. This location provides numerous opportunities to work closely and to share ideas with researchers in the College of Agriculture, the OSU Cooperative Extension Service, the U. S. D. A. - Agricultural Research Service, the Farm Science Review of Ohio as well as the College of Engineering. A series of tasks were continued to transfer and disseminate information developed by researchers affiliated with the Water Resources Center to a wide range of state, federal, county and municipal agencies, the private sector, the academic community and private citizens throughout Ohio.

Water Luncheon Seminar

The Water Resources Center co-sponsors programs throughout the academic year to the water resources community in central Ohio. These programs are developed cooperatively with The Ohio Department of Natural Resources (ODNR), the Ohio Environmental Protection Agency (OEPA), the Natural Resources Conservation Service (NRCS), the District Office of the U. S. Geological Survey (USGS), and the Ohio State University Extension Service. These seminars attract 200 water resources professionals annually from federal, state, county and municipal agencies, the private sector and the academic community. These seminars provide a relaxed forum to discuss current state, federal, and local water policy issues, problems, programs and research results. In addition to providing speakers for each sixth meeting, the Water Resources Center provides administrative and financial support for the seminars.

Water Luncheon Seminar FY 1998

Date	Speaker/Agency	Topic
April 14, 1998	Dr. Larry Brown OSU Extension	A Novel Approach to Incorporating Constructed Wetlands into an Economical & Environmentally Friendly Agricultural Production System in the Maumee River Basin
October 20, 1998	Barbara Lubberger Ohio EPA - Division of Drinking and Ground Waters	Ohio Source Water Protection Program
January 20, 1999	Dr. Harold Walker	Mitigation of Acid Mine Drainage Using FGD Material: Water Quality Aspects

Other Conferences and Seminars the Water Resources Center Co-Sponsored or Supported in FY 1998

Date	Program	Co-Sponsors
March 10-12, 1998	Project WET Facilitator Training @ Round Lake	Ohio Water Education Program
June 9, 1999	WMAO Spring Conference - GIS	Water Management Association of Ohio
September 25-26, 1998	Advanced Leadership Workshop Training: Watersheds	Ohio Water Education Program Cuyahoga Valley Environmental Education Center
October 16, 1998	Environmental Education Programs/Opportunities for Classroom Implementation	Central Ohio Teachers' Association
November 17-19, 1998	Water Management Association of Ohio Annual Conference	Water Management Association of Ohio

The Center's Director continued meeting with the leading state water resources officials to share information on current water management and policy issues; and to seek continued support for our water research program and disseminating the information and technology developed through this program and others at the universities throughout the state and region. A third of the phone calls to the Center are public information calls requesting information on water quality issues.

Researchers have presented their initial findings at national meetings as indicated by the list of abstracts in Part C. Both professors and students have participated in information dissemination at regional, national and international conferences including the SETAC National Meeting, American Chemical Society National Meeting, and the ASAE Conference in St. Joseph, MI.

The project by Levy, et al. has led to cooperation between Miami University, the U.S. Geological Survey, Water Resources Division in Columbus, Ohio, and the City of Cincinnati. The USGS personnel have been investigating similar questions on the nearby Miami River buried-valley aquifer. The researchers submitted a joint proposal with the USGS and the City of Cincinnati Water Works for funding from the Ohio Water Development Authority that will supplement and expand this research.

In addition to the International professional meeting papers listed elsewhere, researchers on the project by Brown and Batte have made other presentations on the overall project scope, demonstration, monitoring and research plans.

Water Management Association of Ohio (WMAO)

The Water Resources Center continued to be the administrative office for the Water Management Association of Ohio (WMAO). This not-for-profit, 300 member, state-wide organization promotes and supports the development, conservation, control, protection and utilization of the water resources of Ohio for all beneficial purposes. It is the only Ohio professional organization that is solely concerned with managing Ohio's water. The WRC provides staff support, office space and equipment to WMAO as a portion of the information transfer program. This is the second year that the WRC has had a project with WMAO to support the Center's activities on this project.

Ohio Water Education Program (OWEP)

The Ohio Water Education Program (OWEP) began in the Fall of 1992 with the Ohio Department of Natural Resources and the Water Resources Center. A Memorandum of Understanding supporting this project has been signed by the Water Management Association of Ohio/Water Resources Foundation of Ohio, the Ohio Department of Natural resources, the Ohio Environmental Protection Agency and the Water Resources Center. There are two functions to this program. The first provides a database of water education materials, projects, and supplies available for water education in Ohio. The second segment of this project is sponsoring Project WET - Water Education for Teachers. This is a national program for students in grades K-12 for interdisciplinary water resources education. The Center has donated office space, telephone and fax facilities, supplies and provides substantial administrative support and services for this project. This project is a major part of the Center's information transfer program.

Two leadership training workshops were held in FY 1998 providing educators with information on Project WET. More than 60 teachers attended these two-day training workshops which consisted of hands-on projects. In the fiscal year there were 47 six hour Project WET workshops held in Ohio where 985 people received instruction and materials on Project WET. Since the program's inception in 1995, more than 6,000 teachers have been trained in 350 workshops. The number of Ohio students exposed to water education is at least 150,000 if you estimate each teacher reaches 25 students annually.

In addition to providing administrative support, the Center staff gave numerous promotion presentations and demonstrations for the program. Further support to this activity was provided through the Water Resources Foundation of Ohio.

Cooperative Arrangements

Section 104 of the Water Resources Research Act directs the Secretary of the Interior to administer program grants to Institutes and Centers established within the States and certain other similar jurisdictions for research, information transfer, and training that will assist the Nation in augmenting water-resources science and technology. Responsibility for administration of this program has been delegated to the U. S. Geological Survey (USGS).

Congressional conference committee language has changed the way Federal funds were awarded under the State Water Institute Program in fiscal year (FY) 1996. Funds will be awarded in two separate parts. One part directed a base grant ($20,000) for each Institute ($1.1 million) while the other part created a competitive grant program for the remaining funds ($3.22 million). The Regional Competitive Grant Program (RCGP) application/solicitation review and selection process was coordinated by a lead Institute in each of four Regions.

The Ohio State Water Resources Research Program in Fiscal Year 1998 began with a Call for Pre-Proposals mailed to administrators and qualified faculty investigators at more than 40 private and public colleges and universities throughout Ohio. This announcement contained the research priorities identified for the 13-state North Central Region that was created by newly enacted legislation.

Of the 500 proposal packages mailed to potential investigators, there were 8 preliminary proposals submitted from four universities in Ohio. Central State University, an historically black university, was one of the colleges to which materials were sent, but they did not submit any preproposals.

Eight pre-proposals from four universities throughout the state were submitted for evaluation and consideration. These pre-proposals were subjected to a review by all of the members of the Water Resources Center's Advisory Committee. In addition, these pre-proposals were distributed to the various divisions within the principal state and federal water-related agencies in the State who serve on the Advisory Committee and their respective divisions reviewed the proposals. The four agencies included in this evaluation were the Ohio Department of Natural Resources, the Ohio Environmental Protection Agency, the District Office of the United States Geological Survey and the Agricultural Research Service in the United States Department of Agriculture.

The results of these reviews were presented at a meeting of the Advisory Committee where this panel selected four of the pre-proposals and instructed the Center's Director to request fully developed proposals from the investigators for submission to the North Central Region Competition. Of these selected pre-proposals, all four were from The Ohio State University.

The four selected pre-proposals were developed more fully and were submitted as full proposals to Nebraska to the North Central Region for competition with projects from each of the other 12 states in the region. Four proposals was the maximum number any state could submit to the regional competition. All of the proposals submitted to the Region were distributed to technical reviewers throughout the nation and ranked according to the total points indicated by the technical reviews. The top twenty-five ranked projects in the region were then distributed to the Directors' through the region for review (a week later the other 25 projects were also distributed with their rankings and reviewers comments.)

The Directors considered the technical rankings, priorities of the region, fiscal budgets, thoroughness of the application, training and professional level of the principal investigator as they selected the top 15 projects to award. Ohio had four projects in the top 25 projects. All four of the projects submitted by Ohio ultimately received funding. Ohio is the only state in the region to have had all four proposals awarded in one year Those projects were: Sonochemical Remediation of PCB Contaminated Sediments by Linda Weavers; In-situ Destruction of Solvents by Permanganate Oxidation by Frank Schwartz; Nutrient Cycling in Integrated Crop/Wetland/Reservoir Management Systems by Larry Brown, Scot Subler; and Enhanced removal of DBP Precursors During Precipitative Softening Through Co-Adsorption Processes by Harold Walker.

The Water Resources Center Director contacts the Principal Investigators on their research projects to discuss progress, budgetary activity and future activities. Progress Reports or Completion Reports are prepared by the Principal Investigator. The investigators are urged to publish the results of their findings in the technical literature of their major disciplines and in other journals that are appropriate to the topic of their research. They are also encouraged and invited to present their findings at the Water Luncheon Seminar that is a part of the information transfer program.

Regional Cooperative Initiatives

The Ohio State University continues as a Charter Member of the Ohio River Basin Research and Education Consortium and the Director of the Water Resources Center has continued to serve as one of the University's three representatives to the Consortium. The Director is a member of the Universities Council on Water Resources and participates in the regional and national meetings of the National Institutes for Water Resources. He is active as the regional representative to the NIWR Executive Board for the Great Lakes region.

Water Resources Center Advisory Committee

College of Engineering

Dr. L. S. Fan
Chair, Chemical Engineering

Dr. E. Earl Whitlatch
Director, Water Resources Center

School of Architecture

Dr. Steven I. Gordon
City and Regional Planning

Professor John W. Simpson
Landscape Architecture

College of Mathematical and Physical Sciences

Dr. E. Scott Bair
Geological Sciences Department

College of Agriculture

School of Natural Resources

Dr. Robert L. Vertrees
Resource Management

Ohio Environmental Protection Agency

Dr. John Estenik

Ohio Department of Natural Resources

Michele Willis, Chief
Division of Water

United States Geological Survey

Steve Hindall
District Chief

United States Department of Agriculture

Dr. Norman Fausey
Agricultural Research Service

E. Student Support

Training Accomplishments

Field of Study	Undergraduate	Masters	Ph. D.	Total
Food, Agricultural & Biological Engineering	5	2	1	8
Agriculture, Environment & Dev. Economics		1		1
Chemical Engineering	1			1
Civil & Environmental Engineering & Geodetic Science	1	1	1	3
Environmental Sciences	2	2	2	6
Geological Sciences	3	3	3	9
Microbiology	2	1		3
Totals	14	10	7	31

These research activities were accomplished with only RCGP Awards. The Base Grant has not been used in these activities but to continue the strong Information Transfer program of the Water Resources Center.

G. Notable Achievements and Awards

In April 1997, A. J. Rossman, one of the graduate students working on Dr. Levy's project submitted a proposal to the Geological Society of America for funding of graduate-student research associated with this project. He was awarded $1,800 and his proposed research, which was closely connected with the research proposed in this project, was also one of 34 out of 478 to receive special recognition as having exceptional merit in concept and presentation.

In early 1997, Penney Miller, one of the graduate students working on this project, submitted a proposal to the United States Environmental Protection Agency for the Science to Achieve Results (STAR) Graduate Student Fellowship to support her research and graduate studies. The STAR program was initiated in 1995 to encourage promising students in their academic and research pursuits in environmentally related fields. This fellowship, which is renewed annually according to a student's progress, offers up to three years of support. Penney was notified of her acceptance into the program in August of 1997 and is one of a hundred people across the nation chosen to receive this award.

In 1998, Penney Miller also was awarded the 1998 Environmental Chemistry Division of the American Chemical Society Graduate Student Award. more than 2,000 students applied for this prestigious award and it was awarded to only fifteen people.

In 1998 Dr. Larry Brown received follow on funding on his reseach from the Ohio Sea Grant for $20,000 and from the USACOE for $25,000. Also Dr. Ollie Tuovinen of the Microbiology Department was awarded a project to study atrazine at the research sites of Dr. Brown's projects.

IN September 1998, Y.P. Chin received follow on funding for three years for $191,950. his project, by the U. S. DOE, EMSP program.

Jonathan Levy also received follow on funding from the Ohio Water Development Authority for a research project with USGS and the City of Cincinnati for $46,900.